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JUNE 1959
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TEXTILE RESEARCH JOURNAL

Frictional Measurements on Fibrous Materials

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Abstract

A method for measuring the coefficient of static friction is described. Results obtained on various materials are given. A statistical analysis of the relationship between frictional force and normal load does not confirm the empirical equations given by other workers, but leads to a quadratic formula.

Introduction

The classical laws of static friction, generally ascribed to the French physicist Amontons, are that the frictional force W is independent of the area of contact between the two sliding bodies and the frictional force W is proportional to the normal load N on the area of contact; by definition, the coefficient of static friction $\mu_s = W/N$. Bowden and coworkers [4] developed a cohesion theory of friction. For the friction between two metallic surfaces, this theory assumes that even a highly polished surface contains asperities with a difference in height equal to the dimension of several hundreds of molecules. When two of these surfaces are brought together, the first contact will be made on the tops of these asperities, with a very small total area. When a load N is applied, the pressure on this area can exceed the yield value p_y of the material, and plastic deformation will occur, resulting in an increased area of contact and a corresponding reduction of the pressure.

This process continues until an area of contact A is attained, given by $p_y = N/A$.

In this phase the contact between the two surfaces is so intense that a strong cohesion between them occurs; they may behave as if they were welded together at the points of contact. To move one surface over the other, a tangential force S is needed to tear up these contacts, and a certain force P must be applied to "plough" the asperities of one surface through the other. The value of the frictional force is then given by $W = S + P$.

In the case of friction between two metallic surfaces, small loads lead to the occurrence of plastic deformation. Lincoln [17], however, pointed out that this need not be necessary for materials with a higher yield value. At low values of the load N, the area of contact proved to be proportional to $N^{2/3}$, this result being in accordance with the calculations of Herz [11]. Also, Lincoln could not establish any evidence for the existence of other cohesional forces than those given by the shear strength of the material; this points to the fact that no "ploughing" occurs in the weaker material.

According to Howell [12, 13, 14], the difference between metallic friction and fiber friction is given

by the fact that for the same value of the load, fibers show a much stronger elastic deformation; a much higher load is needed to attain the yield value of the material, that is to say, to make a contact between two fibers. The laws of Amontons, therefore, have no validity for fibers.

For the frictional force between fibrous materials, Howell and others [5, 12, 17] give the empirical formula $W = aN^b$, where a is dependent on the mechanical properties of the material and b on the nature of the deformation.

An ideally elastic material would give $W = aN^{2/3}$; for the friction between fibers the value of b is given by $2/3 < b < 1$. According to these results the deformation of a fibrous material would be neither ideally elastic nor purely plastic.

Howell and Mazur [15] pointed out that, with the formula $W = aN^b$, the first law of Amontons is a logical consequence of the second; it is valid only when $b = 1$.

Lincoln [18] proved that, even when a purely elastic deformation occurs, the value of b can be higher than 2/3; for two cases, assuming an ideally elastic deformation, he calculated the frictional force W to be proportional to $N^{8/9}$. The occurrence of elastic or plastic deformation depends on the dimensions and the distribution of the asperities [19]. Archard [3] showed the importance of the distribution of the height of these asperities.

Gralén [8] gave another formula, $W = cN + dN^{1-\beta}$, where $1 > \beta \geq 0$.

Various other workers [10, 24, 26, 28, 33] used a linear relationship between W and N.

For our measurements, a modification of the Cambridge Textile Extensometer [32] was made. Figure 1 illustrates the principle of the modified instrument. The method is analogous to that given by Lord [20].

Spring C is connected with a table T_1, rotating at O; c_1 and c_2 are two contacts. A second table T_2, situated at the same level as T_1, is connected with rod K (K lies in the same horizontal plane as C, T_1, and T_2 but is drawn lower for the sake of clearness). At table T_2 a comb k_1 is attached with the aid of a spring, in which comb a fringe f_1, consisting of parallel fibers, is fitted.

On fringe f_1 a similar fringe f_2 is mounted, fitted to comb k_2, attached to table T_1. On top of fringe f_2 a third fringe f_3 is mounted, attached to comb k_3. Atop of these three fringes is placed a small plate Q that can be submitted to a certain load with the aid of a hook and a small tray in which the desired weight S is placed. A small clip V falls behind k_1 and k_3, fixing the position of these two combs with regard to Q. A handle U facilitates the handling of Q.

The dimensions of Q in our experiments were 1×1 cm., which results in an apparent area of contact between the fringes of 1 cm.^{2} The real area of contact depends on various factors; e.g., on the magnitude of the weight S and the fibrous material tested. The total fringe area is about $4 \times 2 = 8$ cm.^{2} The dimensions of Q are small in comparison with those of the total fringe area; these latter, therefore, are not critical.

When the three fringes of fibers are pressed together with a certain load, contact c_2 is closed, motor W_2 starts running at a constant speed, and spring C is extended. The distance between the contacts c_1 and c_2 is as small as possible, so that

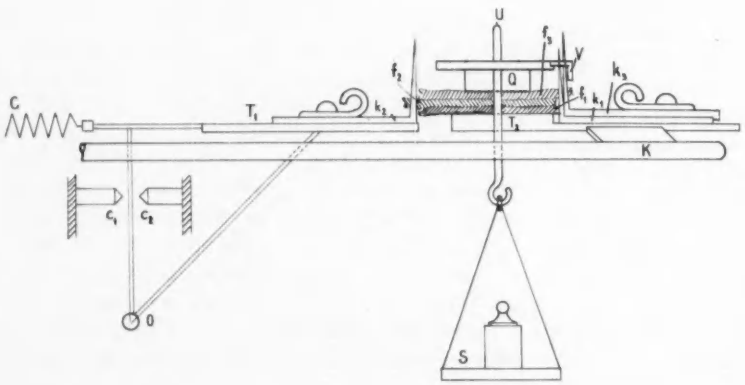

Fig. 1. Principle of the measurement of static fiber friction.

the left contact c_1 is immediately closed by the displacement of T_1. This enables motor W_1 to rotate, resulting in a displacement of K, T_2, f_1, and f_3 to the right. As long as the frictional force between the fringes dominates over the force given by spring C, this same movement is made by table T_1 and fringe f_2. The mutual situation of the fringes, therefore, is not altered. The contact at c_1 is then closed again; this closing and opening continues until the mutual friction between the fringes equals the force given by the extension of spring C. At this moment the left contact c_1 stays closed. K moves to the right and with K a recording drum F. The displacement of this drum, being small at first, is enlarged, and the curve on drum F is deflected. This continues until the displacement of K closes a second contact c, stopping motor W_1 and drum F. After this the curve shows only the extension of C by motor W_2.

Figure 2 shows a diagram of a curve obtained in this way (Curve a). By the use of a suitable gearing it is possible to register the displacement of K with a magnification of 5×; actually it amounts to only a few millimeters.

A certain force is needed for the movement of T_1 and the closing of contact c_1, so that the extension of C (Curve a) must be reduced to that needed to close contact c_1 when no fibrous material is present (Curve b). The distance d in Figure 2 is a measure for the force needed to pull fringe f_2 out of fringes f_1 and f_3 (i.e., the coefficient of friction of the material). The distance d is determined without fringe f_2, but the weight of this fringe (± 50 mg.) is negligible with regard to the weight of T_1. The vertical displacement of T_1 is very small because the gap between c_1 and c_2 is kept as narrow as possible. Inertia effects of T_1 are negligible in comparison with the frictional forces measured and the variation between the measurements.

This method, therefore, measures the force needed to move a fringe of fibers out of two adjacent fringes; contrary to the method described by Lord, in our measurements two areas of contact, instead of one, are used. The coefficient of static friction at a normal load N, therefore, is given by $\mu_N = W/2N$.

The preparation of the fringes was as follows. The material is parallelized by forming a small sliver of about 100 mg. of fibers, dividing this sliver in two parts by pulling at both ends, and again combining these two parts. This is repeated 5 times, after which the fibers are transferred into a small comb, repeatedly combed out with a second comb, and finally divided in about the same quantity (50 mg.) over both combs. In the same way 50 mg. of the material is transferred into a third comb with the aid of a similar comb which is not used at the measurements proper. This method is analogous to the preparation of fibers for the well-known Fibrograph test.

The fringe of fibers in every comb is now laid down on a small cutting table and cut off at a length of 20 mm.; i.e., the distance between the teeth of the left-hand comb and the both right-hand combs when placed in the extensometer.

When the combs are put in the instrument the fibers extending at both sides of the combs are trimmed off and the measurements are started.

This modification of Lord's method has an advantage over the original procedure in that it enables us to register the value of the force continuously. It is possible to measure the maximum value of this force in a much simpler way than by using Lord's method; moreover it is very easy to observe the occurrence of stick-slip effects.

The weight of plate Q with clips and tray amounted to 53.14 g.; the speed of carriage H over lead screw D was 2.73 cm./min. and is higher than that applied by Lord (viz. about 1.27 cm./min.).

On every sample 5–10 measurements were carried out; the number of tests N is given by

$$N = \left(\frac{tV}{E}\right)^2$$

where $t = 1.960$ (for the 95% probability level chosen); $E = 2.5$ (the allowable random sampling error of the mean is then lower than 2.5%); and V = coefficient of variation.

The statistical calculations on our results made it necessary to use 5 or 10 measurements for every N value. This requirement could be met only when 10 measurements were carried out at each N value; if not, only the first 5 results at every load value were used.

The Influence of the Dimensions of Plate Q on the Frictional Force

To establish this influence, the frictional force was measured at three different areas of Q (1.0, 1.5, and 2.0 cm.²) using two different loads (103.1 and 645.1 g.; for sample d, 53.14 and 645.1 g.).

TABLE I. Mean Values of the Frictional Force and the Confidence Interval of This Mean at a Probability Level of 95% for Four Materials at Three Different Areas of Contact and Two Values of the Normal Load

		Total load, g.					
		103.1 (d–53.14)			645.1		
Sample	Area Q, cm.²	Number of observations	Frictional force, g.	Confidence interval, g.	Number of observations	Frictional force, g.	Confidence interval, g.
a	1.0	10	24.3	±1.3	10	201	±7
	1.5	9	21.8	±1.4	7	226	±5
	2.0	10	27.4	±1.2	5	231	±3
b	1.0	10	20.4	±0.7	7	195	±4
	1.5	10	25.1	±1.8	5	203	±5
	2.0	10	27.5	±1.2	6	215	±5
c	1.0	10	25.1	±1.0	10	216	±7
	1.5	10	29.3	±1.5	5	231	±2
	2.0	10	32.3	±2.5	5	237	±3
d	1.0	10	32.2	±1.8	10	175	±9
	1.5	10	32	±2.9	10	187	±5
	2.0	10	34.2	±2.4	10	200	±9

Three cottons (a, b, c) and one wool sample (d) were tested; Table I gives the mean value of the frictional force measured and the confidence interval of this mean at a probability level of 95%.

Except in two cases the frictional force increases with increasing area Q, i.e., with an increase of the apparent area of contact. This fact does not agree with Lord's results, which indicated that the frictional force was independent of this area. These results, however, are in contradiction with the formula $W = aN^b$, applied by Lord for the relationship between the frictional force W and the normal load N.

When the formula $W = aN^b$ is used, the frictional force is independent of the apparent area of contact only for the case that $b = 1$.

For an apparent area of contact = 1 cm.² the frictional force is given by

$$W_1 = aN_1^b \tag{1}$$

Applying this same load N_1 on an area of x cm.² gives a normal load per square centimeter of this area

$$N/\text{cm.}^2 = \frac{N_1}{x} \tag{2}$$

assuming a linear relationship between the actual and the apparent area of contact. The frictional force per square centimeter under a total area of x mc.² is given by the equation

$$W_{x,1} = a\left(\frac{N_1}{x}\right)^b \tag{3}$$

and for a total area of x cm.² the frictional force is given by

$$W_x = xW_{x,1} = xa\left(\frac{N_1}{x}\right)^b$$

$$= aN_1^b \cdot x^{1-b} = W_1 \cdot x^{1-b} \tag{4}$$

The ratio between the frictional force W_x at an apparent area of contact of x cm.² and the frictional force W_1 at an apparent area of contact of 1 cm.² is then given by

$$\frac{W_x}{W_1} = x^{1-b} \tag{5}$$

which formula shows that only in the case that $b = 1$ are the forces W_x and W_1 equal.

This result proves that the first law of Amontons is a logical consequence of the second [14]: for $b < 1$, W increases with increasing x.

The contradiction in Lord's results is that on the one hand the formula $W = aN^b$ is applied, while on the other hand no relation between the frictional force and the apparent area of contact could be established.

We must take into account this relationship between frictional force and the area of plate Q. All our measurements, therefore, were carried out at

TABLE II. Fiber Properties of 12 Cotton Samples

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Origin	Egypt	Peru	Memphis	Argent.	Brazil	Egypt	Peru	Calif.	Congo	Congo	Peru	Memphis
Variety	Gizeh −30	Pima	—	—	—	Karnak	Tanguis	Acala 4–42	Kogar	Stonor	Pima	—
Upper half mean, in.*	1.15	1.29	1.08	.98	.99	1.32	1.16	1.16	.97	.96	1.30	1.09
Mean, in.*	.92	.98	.84	.78	.80	1.03	.90	.94	.78	.77	1.02	.86
Uniformity ratio, %*	80.0	76.0	78.0	79.5	81.0	78.0	78.0	81.0	80.0	80.0	79.0	79.0
Micronaire index, F_m	4.00	3.25	4.35	3.70	4.20	3.85	5.50	4.00	4.10	3.40	3.45	5.00
Micronaire maturity, R_c, %	80.0	71.5	79.0	76.0	78.0	78.0	86.5	77.5	78.0	72.5	75.0	83.5
Causticaire fineness, F_c, μg./in.	3.90	3.25	4.45	3.75	4.35	3.75	5.05	4.10	4.20	3.60	3.25	4.80
Wax on fiber, w_1, %†	.55	.59	.44	.49	.47	.48	.42	.58	.48	.50	.59	.38
Wax/unit length, w_2, μg./in.‡	2.14	1.92	1.96	1.84	2.04	1.80	2.12	2.37	2.01	1.80	1.92	1.82
Clegg maturity, R_x, %	85.5	61.1	77.5	61.1	71.2	85.4	80.3	69.1	78.6	57.4	78.4	81.4
Half-convolutions of fiber/cm., w**	36.8	30.0	38.7	38.1	57.4	36.5	50.5	47.4	44.4	59.4	38.8	63.2
Coefficient of variation of w, %	41.3	47.3	33.6	54.6	30.0	34.5	36.0	29.1	38.5	38.2	49.0	28.3
Hairweight, h, μg./in.	4.26	2.97	4.14	3.34	4.13	3.26	4.98	3.51	3.92	3.37	2.62	4.26
Wax/unit length, w_3, μg./in.††	2.35	1.75	1.82	1.64	1.94	1.56	2.09	2.04	1.98	1.68	1.55	1.62
Micronaire index at linear scale, F_1	3.90	2.85	4.30	3.50	4.10	3.70	5.40	3.90	4.00	3.10	3.15	4.95
Wax/unit of fiber surface, w_4‡‡	2.14	1.68	1.89	1.72	1.92	1.78	2.26	2.26	1.92	1.55	1.86	1.88
$1/F_1$	.256	.350	.232	.285	.245	.270	.185	.256	.250	.323	.318	.202
F_1 measured after fiber swelling in 18% NaOH, F_1'	5.60	4.35	5.95	5.25	5.90	5.40	6.40	5.70	5.75	5.15	4.95	6.10
$1/F_1'$	.179	.206	.169	.190	.170	.185	.156	.175	.174	.194	.202	.164
Pressley Index at zero gauge length	8.8	8.2	8.1	6.9	6.8	9.5	7.1	7.4	7.1	7.1	8.3	7.9

* As measured by the Spinlab Fibrograph (manufactured by Special Instruments Laboratories, Knoxville, Tenn.).
† Determined by extraction of the material with boiling ether in a Soxhlet apparatus for 2 hr.
‡ $w_2 = (w_1/100) \times F_c$.
** Measured microscopically by counting at a 1-cm. length midway of 25 fibers per sample.
†† $w_3 = (w_1/100) \times h$.
‡‡ $w_4 \propto w_1 \times F_1$.

an apparent area of contact of 1 cm.² between the fringes.

All fiber samples were tested in the standard atmosphere; 21 ± 1° C. and 65 ± 1% RH.

Measurements on 12 Cotton Samples

The following cotton samples were tested after being opened on a Shirley Analyser.

1. Giza—30
2. Peruvian Pima
3. Memphis
4. Argentine
5. Brazilian
6. Karnak
7. Peruvian Tanguis
8. Acala 4–42
9. Congo Kogar
10. Congo Stonor
11. Peruvian Pima
12. Memphis

The results obtained were used primarily to decide in which way the relation between the frictional force W and the load N had to be represented. As already described, two formulas must be considered in this respect: the linear model ($W = aN + b$) and the exponential model ($W = cN^d$ or $\log W = \log c + d \log N$).

In order to verify which gave the most exact reflection of our results, the linear regression was tested against a nonlinear (quadratic) regression for both models [23].

This method is based on the testing of the hypothesis

$$H_0 : \alpha_3 = 0 \tag{6}$$

for the model

$$y = \alpha_1 + \alpha_2 v_r + \alpha_3 z_r \tag{7}$$

where $\nu = 1, \cdots, n$ (n = total number of observations), $v = x - \bar{x}$ and $z = x^2 - \overline{x^2}$ ($\bar{x}$ and $\overline{x^2}$ are subtracted to simplify the calculation) for $y = W$ and $x = N$, as for $y = \log W$ and $x = \log N$.

A direct testing of the linear against the logarithmic model would have been more ideal, but this test is not yet available.

The test gives an indication about the acceptability of a way of representing the experimental results. The formula which stands the test $H_0 : \alpha_3 = 0$ the best is then chosen as the most representative for the relation between W and N.

TABLE III. Values of $k(t)$ for 12 Cotton Samples; 17 Degrees of Freedom

Sample	Linear model $k(t)$	Logarithmic model $k(t)$
1	0.3–0.4	0.4 –0.5
2	0.02	0.3
3	0.4–0.5	0.01
4	0.3–0.4	0.6 –0.7
5	0.3–0.4	0.01
6	0.1–0.2	0.2
7	0.9–1.0	0.01–0.02
8	0.2–0.3	0.8
9	0.3	0.3
10	0.3	0.3 –0.4
11	0.2	0.2 –0.3
12	0.9–1.0	0.02–0.05

TABLE IV. Values of $k(t)$ for 8 Different Fibrous Materials

Sample	Degrees of freedom	Linear model $k(t)$	Logarithmic model $k(t)$
33 Cupr. amm. rayon	37	0.6–0.7	0.01
34 PAN	37	0.3–0.4	0.1 –0.2
35 Nymcrylon	37	0.3	0.001
36 Enkalon	37	0.005	0.001
37 Terlenka	37	0.01	0.2 –0.3
38 Dynel	37	0.001	0.01–0.001
39 Merino	33	0.5–0.6	0.001
40 Crossbred	17	0.8–0.9	0.001

TABLE V. Micronaire Values and Causticaire Maturity of 6 Cotton Samples

Sample	F_m, μg./in.	R_c, %	F_1
13 Rio Grande	3.50	—	3.20
14 Rio Grande	4.50	—	4.45
15 Rio Grande	5.10	—	5.05
16 Mexicali	2.50	57.5	1.20
17 Mexicali	3.50	70.0	3.20
18 Mexicali	5.15	86.0	5.10

The calculation is based on a statistic t possessing a Student distribution with $N - 3$ degrees of freedom.

Table III gives calculated values where $k(t)$ is defined as the size of the smallest critical region containing the observed value t in relation to H_0 for the linear and the logarithmic model. The values of $k(t)$ are drawn from the tables of Pearson and Hartley [27].

Where in all these cases the coefficient of regression of log W had a value between 0.9 and 1.0, the exponential (or logarithmic) model was almost a linear model. For $d = 1$ this would have been completely so; only a small difference between both models, therefore, could be expected.

For this reason the results obtained on some fibrous materials having a lower coefficient of regression were also tested in this way (Table IV).

From Table IV it can be seen that the linear model must be preferred to the logarithmic model; in most cases $k(t)$ is greater for the linear model. The character of $k(t)$, however, is such that this linear model also does not agree sufficiently with our results.

For all calculations, therefore, a quadratic instead of a linear model was used:

$$y = \alpha_1 + \alpha_2 v_\nu + \alpha_3 z_\nu \tag{7}$$

This quadratic model is not yet ideal, but agrees in such a way with the results that the calculation of a curve of higher degree would not have been of much practical importance.

Besides the 12 fiber samples used in the analysis mentioned above, 6 other cotton samples (3 Rio Grande and 3 Mexicali) differing strongly in Micronaire value were tested (Table V).

The calculated estimations a_1, a_2, and a_3 of α_1, α_2, and α_3, respectively, gave an equation

$$W = a_1 + a_2(N - \bar{N}) + a_3\{(N - \bar{N})^2 - \overline{(N - \bar{N})^2}\} \tag{8}$$

for every sample tested.

To attain a sufficient extension of the spring it was necessary to test every sample at various N values, which causes a dependability of the factors a_1, a_2, and a_3 on the mean load value $\bar{N}$.

Equation 8, therefore, was rewritten as

$$W = A_1 + A_2 N + A_3 N^2 \tag{9}$$

where

$$A_1 = a_1 - a_2\bar{N} - a_3\{\overline{(N - \bar{N})^2} - \overline{N^2}\}$$
$$A_2 = a_2 - 2a_3\bar{N}$$

and

$$A_3 = a_3$$

Equation 9 enables us to calculate the value of W at any value of N. This equation is valid only within the range of loads applied in our experiments; that is, between 50 and 900 g.

For two N values arbitrarily chosen within this range (300 g. and 600 g.) we calculated the value of W; dividing by $2N$ (in our experiments we use two areas of contact) gives the coefficient of static friction μ_s.

Moreover, it seemed of interest to calculate the direction of the tangent of the W–N curve at a certain load; this factor is expressed in a directional coefficient β and calculated from

TABLE VI. Values of A_1, A_2, A_3, W, μ, and β for 18 Cotton Samples at Two Different Load Values

Sample	A_1, g.	A_2	$A_3 \times 10^6$, g.$^{-1}$	N = 300 g. W_{300}, g.	μ_{300}	β_{300}	N = 600 g. W_{600}, g.	μ_{600}	β_{600}
1	+ 5.3	0.611	− 36.8	185.2	0.309	0.589	358.6	0.299	0.567
2	− 0.6	0.651	− 65.7	189.2	0.315	0.612	366.7	0.305	0.572
3	+ 6.7	0.654	+ 26.5	205.3	0.342	0.670	408.6	0.341	0.686
4	+ 1.5	0.659	− 32.1	196.2	0.327	0.640	385.2	0.321	0.620
5	+10.8	0.625	+ 26.3	200.8	0.335	0.641	395.4	0.329	0.657
6	+ 4.7	0.604	− 48.3	181.5	0.303	0.575	349.6	0.291	0.546
7	+10.2	0.644	− 2.7	203.3	0.339	0.642	395.7	0.330	0.641
8	+ 1.3	0.681	− 42.4	201.7	0.336	0.656	394.5	0.329	0.630
9	+ 3.8	0.684	− 55.9	203.9	0.340	0.650	394.0	0.328	0.617
10	+ 3.9	0.671	− 31.2	202.4	0.337	0.652	395.3	0.329	0.634
11	+ 4.1	0.619	− 45.2	185.6	0.310	0.592	359.1	0.299	0.565
12	+ 7.0	0.624	+ 2.5	194.5	0.324	0.622	382.4	0.319	0.627
13	+ 9.1	0.528	+214.3	186.9	0.311	0.657	403.1	0.336	0.785
14	+ 3.3	0.712	− 69.6	210.6	0.351	0.670	405.4	0.338	0.628
15	+ 5.8	0.684	− 9.3	210.0	0.350	0.678	412.7	0.344	0.673
16	+ 2.4	0.652	− 70.4	205.3	0.341	0.694	419.9	0.349	0.736
17	+ 4.2	0.659	+ 26.2	204.2	0.340	0.675	409.0	0.341	0.690
18	+ 4.4	0.696	+ 1.8	213.4	0.356	0.697	422.7	0.352	0.698

TABLE VII. Calculated Values of S and $k(t)$ for the Correlation Between Some Fiber Properties and the Values of μ and β (Italics indicate correlation on a level of significance >95%)

Fiber property	Number of samples	μ_{300} S	μ_{300} $k(t)$	μ_{600} S	μ_{600} $k(t)$	β_{300} S	β_{300} $k(t)$	β_{600} S	β_{600} $k(t)$	
F_m	18	46	0.09	31	0.26	22	0.43	17	0.55	
F_m − 0.8	18	67	*0.01*	53	0.05	43	0.10	38	0.16	Eg. & Pima − 0.8
F_m	14	23	0.23	−1	1.00	− 3	0.91	−10	0.63	− Eg. & Pima
R_c	15	2	0.96	−1	1.00	−10	0.66	− 2	0.96	
F_c	12	22	0.15	28	0.06	18	0.25	29	*0.04*	
F_1	12	22	0.15	26	0.09	16	0.31	28	0.06	
R_s	12	−17	0.28	−17	0.28	−23	0.13	−15	0.35	
P.I.	12	−33	*0.03*	−33	*0.03*	−27	0.07	−35	*0.02*	
P.I.	8	5	0.61	4	0.72	9	0.32	1	1.00	− Eg. & Pima
w_1	12	−17	0.28	−20	0.20	− 8	0.64	−24	0.12	
w_2	12	10	0.55	16	0.31	12	0.46	8	0.64	
w_3	12	22	0.15	24	0.12	20	0.20	16	0.31	
w_4	12	12	0.46	16	0.31	12	0.46	12	0.46	
w	12	18	0.25	24	0.12	22	0.20	28	0.06	
CV_w	12	− 8	0.64	−18	0.25	−14	0.38	−22	0.15	
h	12	21	0.17	29	0.05	15	0.35	27	0.07	

$$\beta = \frac{dW}{dN} = A_2 + 2A_3N \qquad (10)$$

Table VI gives the values of A_1, A_2, A_3, W, μ, and β for 18 cotton samples for $N = 300$ g. and $N = 600$ g. From the table it is obvious that the samples 1, 2, 6, and 11 (Egyptian Giza—30, Karnak, and Peruvian Pima) show the lowest values of μ and β.

Figure 3 shows the calculated W–N relation for four different cotton samples. It is obvious that the Egyptian cotton possesses a lower μ value for all values of N; the differences between the other samples are only systematic at higher N values.

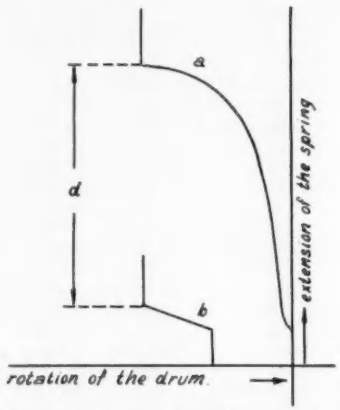

Fig. 2. Schematic diagram of a curve obtained when measuring fiber friction (a) and when no material is present (b). Distance d is a measure for the frictional force between the fringes.

The values of μ_{300}, μ_{600}, β_{300}, and β_{600} were correlated with various fiber properties, using Kendall's rank correlation method. Table VII gives the calculated values of S and $k(t)$.

The coefficient of static friction is correlated only with the Pressley Index of the material. At $N = 300$ g. the Micronaire index F_m also shows a strong correlation, at least when F_m is corrected with a factor -0.8 for the Egyptian and Peruvian Pima samples. According to Abou Sehly, Tallant, and Worner [1], however, this correction is not applicable to all Egyptian cottons.

Of both directional coefficients only β_{600} is strongly correlated with the Pressley Index and the Causticaire fineness of the material.

All correlations mentioned, however, are caused by the different frictional behavior of the Egyptian and Pima samples; when these samples are omitted from our calculations, no correlation is present at all (Figures 4, 5, 6, 7, 8).

It is typical that μ and β generally show a negative correlation with the maturity of the fiber; this correlation is stronger with the Clegg maturity, R_z [7], than with the Causticaire maturity, R_c. This effect is in accordance with Lord's result that a mature fiber shows a lower coefficient of friction than an immature one. Assuming that the friction of a cotton fiber is in the main dependent on the shape of its cross section and the number of convolutions per unit length, one could expect two curves for the relationship between μ and the maturity of the fiber (Figure 9).

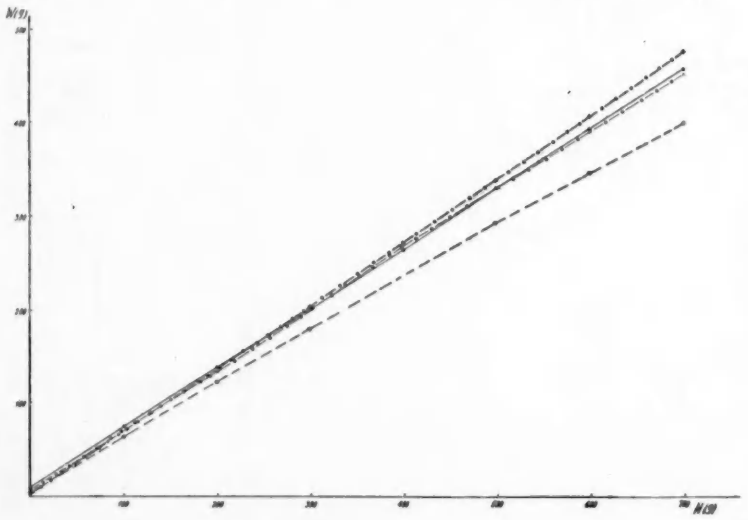

Fig. 3. Calculated W–N relation for four different cottons. ●——●: Peruvian Tanguis, ○——○: Egyptian Karnak, +–●–●–+: Memphis, and ×–○–○–×: Congo Kogar.

Curve 1 shows this relationship if the frictional behavior were dependent only on the shape of the cross section of the fiber, Curve 2 the influence of fiber maturity on μ when only the convolutions of the fiber would play their part. Curve 3 should be expected when both influences act at the same time.

Lord established a relationship between μ and the maturity of the fiber as given by Curve 1; his conclusion, therefore, was that the frictional behavior of the cotton fiber is dependent only on the shape of the cross section. A statistical analysis confirmed this opinion, for the introduction of the number of convolutions in the correlation between maturity and μ did not result in a higher value for the coefficient of correlation.

A further analysis, however, shows this conclusion to be premature; the different behavior of the Egyptian and Peruvian Pima samples in comparison with that of other samples has a distinct influence. Generally the Egyptian samples possess a high R_z value and suggest by their simultaneous low μ values the existence of a certain relationship between μ and R_z for all cottons tested. However, dividing our results according to the different varieties shows the untenability of this relation. Lord's results, when divided in the same way, also show that his conclusion does not hold within the single varieties.

Our measurements of the three Rio Grande and the three Mexicali samples give the same picture: for the samples of one variety, though strongly differing in maturity, the values of μ are practically the same, particularly for μ_{600}. A further argument for this opinion is formed by the results obtained with the two Peruvian Pima samples (R_z values 61.1% and 78.4% respectively), which two samples show practically the same value of μ.

In our opinion, therefore, Lord's conclusion is not justified; just as the negative correlation in our results, it is brought about by the choice of the samples to be tested.

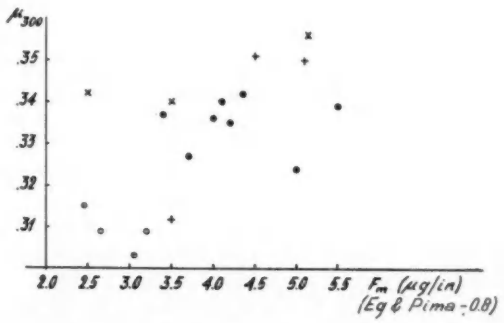

Fig. 4. Relation between the Micronaire value (curvilinear scale) F_m and μ_{300}. ○: Egyptian and Pima samples ($F_m - 0.8$), ●: Upland type, +: Rio Grande, and ×: Mexicali.

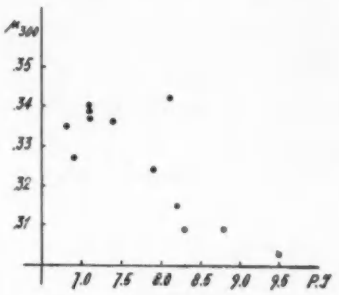

Fig. 5. Relation between the Pressley Index and μ_{300}. ○: Egyptian and Pima samples, ●: Upland type.

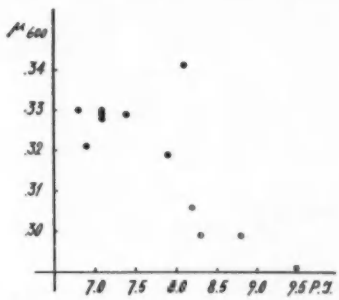

Fig. 6. Relation between the Pressley Index and μ_{600}. ○: Egyptian and Pima samples, ●: Upland type.

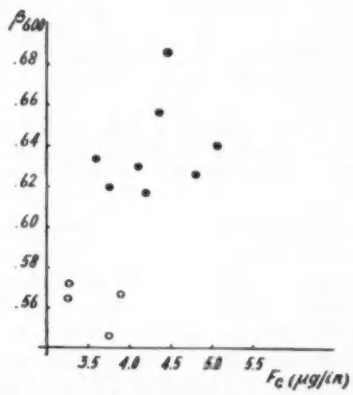

Fig. 7. Relation between the Causticaire Fineness F_c and β_{600}. ○: Egyptian and Pima samples, ●: Upland type.

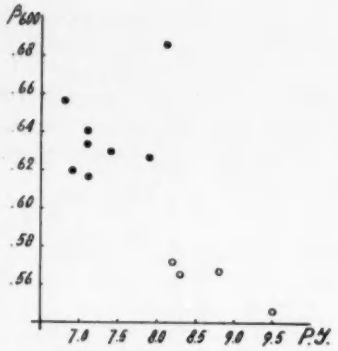

Fig. 8. Relation between the Pressley Index and β_{600}. ○: Egyptian and Pima samples, ●: Upland type.

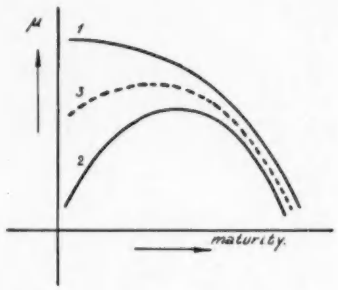

Fig. 9. Possible relation between fiber maturity and μ.

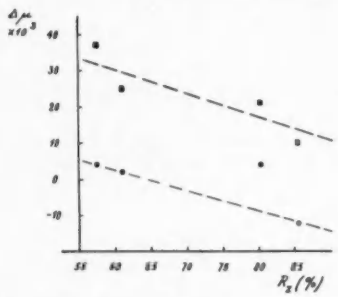

Fig. 10. Relation between the Clegg maturity R_z and $\Delta\mu$ ($= \mu_{normal} - \mu_{mercerised}$). ●: at $N = 300$ g., ■: at $N = 600$ g., ○: Giza-30 at $N = 300$ g., □: Giza-30 at $N = 600$ g.

Both μ and β are positively correlated with w, the number of half-convolutions of the fiber, and negatively correlated with the coefficient of variation CV_w; although these correlations are not statistically significant and therefore cannot be considered as a strong argument, they are in accordance with the results of Adderley [2] and Sen and Ahmad [31].

TABLE VIII. Values of μ for 12 Cotton Samples, Untreated and Mercerized Without Tension

$N = 645.1$ g.

Sample	Untreated	Mercerized	$\Delta\mu$ ($=\mu_{untr.} - \mu_{merc.}$)
1	0.308	0.282	0.026
2	0.308	0.279	0.029
3	0.350	0.307	0.043
4	0.328	0.293	0.035
5	0.336	0.297	0.039
6	0.302	0.285	0.017
7	0.339	0.306	0.033
8	0.336	0.290	0.046
9	0.353	0.288	0.065
10	0.334	0.288	0.046
11	0.307	0.284	0.023
12	0.328	0.313	0.015

Finally, Table VII shows the correlation between μ and β on the one hand and F_c and h on the other hand to be strongest at the highest load value. The difference in frictional behavior between a coarse and a fine fiber, therefore, is greater at the higher load values; the area of contact between the fibers will be less independent of the normal load N as the fineness of the fiber decreases.

Measurements on Various Chemically Treated Cottons

Cotton Mercerized Without Tension

The 12 cotton samples mentioned before, when their Causticaire maturity was established, were treated at room temperature with 18% NaOH without tension and dried. Table VIII gives the results of our measurements on this material at $N = 645.1$ g. It is clear that in all cases the μ value is decreased.

For four of these samples the measurements were carried out at three other values of the load N; the results are given in Table IX. It is evident that the factors A_2 and A_3 differ systematically for the untreated and the treated samples: A_2 increases and A_3 decreases when the material is treated with caustic soda. Although not significantly, the differences $\Delta\mu$ and $\Delta\beta$ are negatively correlated with the Clegg maturity R_z (Figures 10 and 11).

Dewaxed Cotton

Table IX also gives the results obtained on four cotton samples dewaxed by extraction with boiling ether for 3 hr. (viz. the samples 1, 6, 7, and 8).

It is remarkable that for both Egyptian cottons (1 and 6) the value of A_2 increases by this extraction, while A_3 decreases for sample 1 and increases

for the other cottons; for the Egyptian samples (1b and 6b) A_3 is negative, for the samples 7b and 8b, positive. As a consequence hereof the values of μ and β increase by dewaxing (except μ_{300} of sample 8); the W–N curve for these dewaxed cottons is steeper than for the untreated material. This effect is in accordance with the results of Sen and Ahmad [31] for Indian cotton.

A distinct relationship between the percentage wax of the fiber and the increase of μ and β could not be established, although this is probably caused by the different behavior of sample 8 (Acala 4–42).

An interesting point is the different extensometer curve obtained with this dewaxed material. The reason for the change in this curve must be ascribed to the occurrence of the so-called stick-slip effect. The importance of the cotton wax, therefore, is not only that it decreases the coefficient of friction but also that it furthers a more uniform sliding of the fibers along each other, which property is of great importance when the material is passed through a drawing-zone.

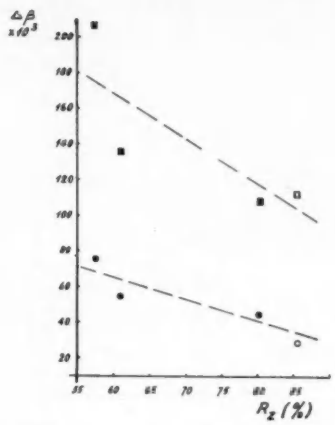

Fig. 11. Relation between the Clegg maturity R_z and $\Delta\beta$ ($= \beta_{normal} - \beta_{mercerized}$). ●: at $N = 300$ g., ■: at $N = 600$ g., ○: Giza-30 at $N = 300$ g., □: Giza-30 at $N = 600$ g.

Scoured Cotton

The same samples (1, 6, 7, and 8) were scoured with 1% NaOH at 115° C. for 8 hr. Table IX shows that, except for sample 1, this scouring increases the values of μ and β more than the dewaxing with ether.

Figures 12 and 13 show the W–N relationship for sample 1 (Giza−30) and sample 7 (Peruvian Tanguis) for 4 cases:

a. untreated,
b. mercerized without tension,
c. dewaxed,
d. scoured.

TABLE IX. Values of μ and β for Some Chemically Treated Cotton Samples

Sample	A_1, g.	A_2	$A_3 \times 10^6$, $g.^{-1}$	μ_{300}	β_{300}	μ_{600}	β_{600}
1	+ 5.3	0.611	− 36.8	0.309	0.589	0.299	0.567
1a*	+10.5	0.664	−174.0	0.323	0.560	0.289	0.455
1b	+ 5.5	0.722	− 68.9	0.360	0.681	0.345	0.639
1c	+11.1	0.603	+ 14.4	0.322	0.612	0.315	0.620
4	+ 1.5	0.659	− 32.1	0.327	0.640	0.321	0.620
4a	+ 4.4	0.686	−168.4	0.325	0.585	0.295	0.484
6	+ 4.7	0.604	− 48.3	0.303	0.575	0.291	0.546
6b	+ 7.4	0.618	− 7.9	0.320	0.613	0.313	0.609
6c	+12.5	0.610	+ 8.8	0.327	0.615	0.318	0.621
7	+10.2	0.644	− 2.7	0.339	0.642	0.330	0.641
7a	+12.6	0.661	−106.7	0.336	0.597	0.309	0.533
7b	+12.6	0.638	+ 53.7	0.348	0.670	0.346	0.702
7c	+ 9.1	0.741	− 81.2	0.374	0.692	0.354	0.644
8	+ 1.3	0.681	− 42.4	0.336	0.656	0.329	0.630
8b	+16.4	0.549	+180.6	0.329	0.657	0.342	0.766
8c	+13.1	0.615	+130.0	0.349	0.693	0.357	0.771
10	+ 3.9	0.671	− 31.2	0.337	0.652	0.329	0.634
10a	+ 4.0	0.727	−249.6	0.333	0.577	0.292	0.427

* a: mercerized without tension, b: dewaxed, c: scoured.

The highest W value for Giza−30 is obtained by ether extraction; for Peruvian Tanguis this is the case when scouring the material.

When mercerizing without tension at lower N values μ is increased; at higher N values μ is much lower than for the untreated material.

Decrystallized Cotton

Table X gives the results obtained on two cotton samples, one decrystallized with the aid of ethylamine, the other consisting of the same material untreated. It is evident that the decrystallized sample shows the highest coefficient of friction; the difference between both samples decreases with increasing value of the load N.

Measurements on Other Fibrous Materials

On 23 different materials the results given in Table XI were obtained; the samples were tested in their technical condition.

Comparison of both viscose rayon fibers Fibrenka and Phrix shows that Fibrenka possesses the highest

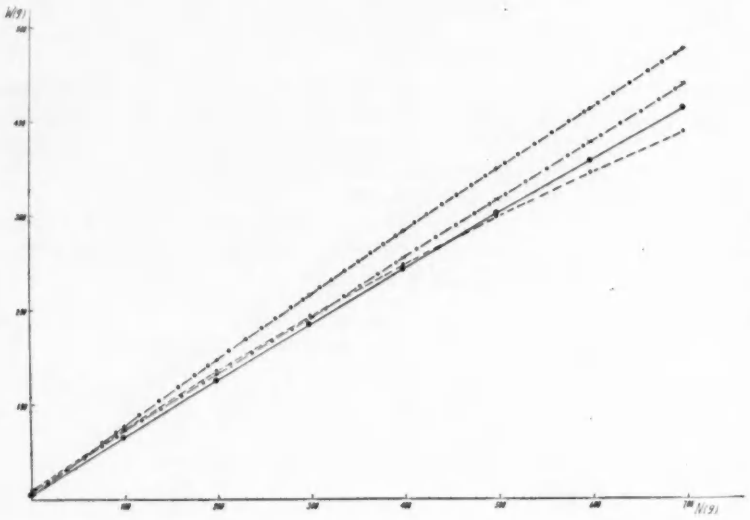

Fig. 12. Calculated values of the frictional force W at various N values for a Giza-30 sample. ●———●: normal, ○———○: mercerized, +–●–●–+: dewaxed, ×–○–○–×: scoured.

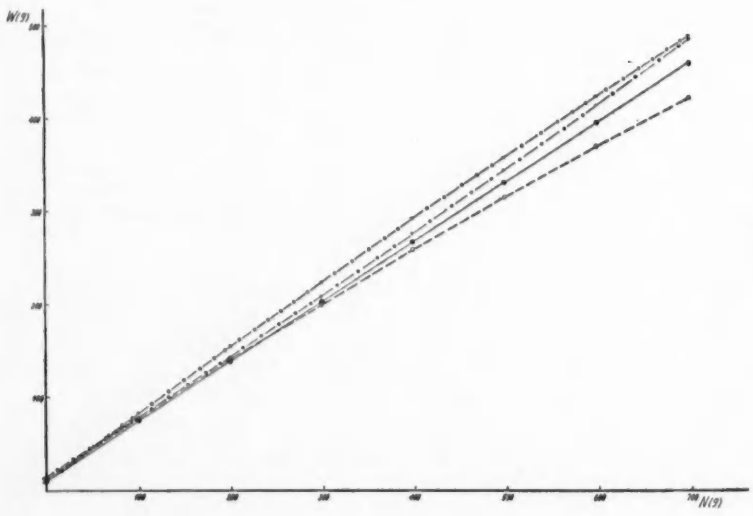

Fig. 13. Calculated values of the frictional force W at various N values for a Peruvian Tanguis sample. ●———●: normal, ○———○: mercerized, +–●–●–+: dewaxed, ×–○–○–×: scoured.

TABLE X. Values of μ and β for an Untreated and a Decrystallized Cotton

Sample	Wax, %	A_1, g.	A_2	$A_3 \times 10^6$, $g.^{-1}$	μ_{300}	β_{300}	μ_{600}	β_{600}
46 Untreated	0.75	14.8	0.538	+170.8	0.320	0.642	0.333	0.745
46d Decrystallized	0.25	12.4	0.786	−140.3	0.393	0.702	0.361	0.618

TABLE XI. Results Obtained on 21 Different Fibrous Materials

Sample	Material	A_1, g.	A_2	$A_3 \times 10^6$, $g.^{-1}$	μ_{300}	β_{300}	μ_{600}	β_{600}
	Viscose rayon							
19	Fibrenka dull 31 mm., 1.5 den.	−11.6	0.794	−195.4	0.348	0.677	0.329	0.560
20	Fibrenka, dull 40 mm., 1.5 den.	−25.2	1.015	−461.3	0.396	0.738	0.348	0.461
21	Fibrenka, dull 62 mm., 3 den.	−17.5	0.940	−289.5	0.397	0.766	0.369	0.593
22	Fibrenka, bright 40 mm., 1.5 den.	− 1.2	0.751	− 38.1	0.368	0.728	0.363	0.705
23	Phrix, dull 62 mm., 2.75 den.	+13.3	0.564	+ 42.3	0.311	0.589	0.306	0.615
24	Phrix, dull 62 mm., 3.75 den., crimped	+20.8	0.545	+123.6	0.326	0.619	0.327	0.693
25	Phrix, dull 60–70 mm., 3.75 den.	+15.0	0.518	+ 50.6	0.292	0.548	0.287	0.579
26	Acetate, dull 60 mm., 3 den.	+ 0.8	1.036	−288.9	0.476	0.863	0.432	0.689
27	Acetate, dull 40 mm., 3 den.	+ 9.1	0.926	−132.5	0.458	0.846	0.431	0.767
28	Cuprammonium rayon	+19.2	0.500	− 27.8	0.278	0.483	0.258	0.467
29	PAN	+12.0	0.622	− 37.7	0.325	0.599	0.310	0.577
30	Nymcrylon	+13.2	0.622	− 38.4	0.327	0.599	0.311	0.576
31	Enkalon	+19.3	0.726	− 73.3	0.384	0.682	0.357	0.638
32	Terlenka	+12.3	0.689	−107.3	0.349	0.625	0.323	0.560
33	Dynel	− 6.1	0.905	−271.3	0.402	0.742	0.366	0.579
34	Merino, scoured	+22.5	0.451	+ 11.1	0.265	0.458	0.248	0.464
35	Crossbred	+17.5	0.502	+ 5.6	0.281	0.505	0.267	0.509
36	Teflon	+ 6.6	0.580	−189.6	0.273	0.466	0.239	0.352
37	Saran	+17.6	0.652	−229.0	0.322	0.515	0.272	0.377
38	Fibravyl	+24.4	0.580	+209.2	0.362	0.706	0.373	0.831
39	Nylon 66	+34.8	0.789	+ 42.2	0.459	0.814	0.436	0.840
40	Enkalon, high tenacity	+13.1	0.836	−102.2	0.425	0.775	0.398	0.713
41	Enkalon, low tenacity	+ 3.6	0.916	−301.2	0.419	0.735	0.371	0.555

coefficient of friction and the highest value of β_{300}. The values of A_2 for Phrix are lower than for Fibrenka; for Phrix A_3 is positive, for Fibrenka negative. For higher N values than were applied in our investigation we may, therefore, expect that the coefficient of friction for Phrix will be higher than that of Fibrenka. It is not impossible that this different frictional behavior must be ascribed to a different method of manufacture or to a difference in finishing agent.

Between the Fibrenka samples the following differences are remarkable.

A coarse fiber generally gives a higher μ and β value than a fine fiber (samples 19 and 20 compared with 21). This relationship between frictional force and denier is in accordance with the positive correlations between F_c and h on the one hand and μ_{300} and μ_{600} on the other, as were found for cotton. Röder [30] established the same influence of the denier for the dynamic coefficient of friction.

A comparison of the μ values of samples 20 and 22 shows that at low N values the bright fiber is smoother than a dull fiber, which effect is contrary

to that at high N values. Röder found the dynamic coefficient of friction of a dull material to be higher than that of a bright fiber.

For the Phrix samples the influence of the fiber denier is not in accordance with that found for the Fibrenka material; it is evident, however, that a strongly crimped fiber possesses a higher coefficient of friction.

The two acetate samples agree only in regard to their μ_{600} value.

Cuprammonium rayon is a much smoother fiber than viscose and acetate, possibly as a result of the more circular cross section of the fiber.

The perfect agreement of PAN and Nymcrylon is remarkable: both are polyacrilonitrile fibers, but of a different manufacture.

Both wool samples 34 and 35 and Teflon show a low value of μ and β; nylon 66, however, possesses a high μ value.

Comparison of a High and Low Tenacity Enkalon Sample

Table XI also shows the results obtained on a high and a low tenacity Enkalon sample. It is evident that, especially at $N = 600$ g., the high tenacity material possesses the highest μ and β values: A_2 is smaller and A_3 is greater than for the low tenacity sample.

Discussion and Summary

Our measurements did not agree sufficiently with the exponential and linear formulas generally given in the literature for the relationship between normal load N and frictional force W. As the result of a statistical analysis we obtained the quadratic formulation $W = A_1 + A_2N + A_3N^2$, where A_1, A_2, and A_3 are constant for a given material.

The reason for this disagreement is probably caused by two circumstances.

1. For our measurements, raw technical material instead of the usual purified fiber was used.

2. Until now there has been no attempt to obtain the most probable model for this relationship with the aid of a statistical analysis.

Differences in Frictional Behavior Among Various Fibrous Materials

For different materials the magnitude of the mutual bonds at the area of contact of the frictional force will be defined by different properties of the chain molecules, such as

a. the attractive energy between these molecules,
b. the elasticity,
c. the degree of orientation.

The influence of the attractive energy between chain molecules, expressed by the molecular cohesion energy M in cal./mole, is given by Table XII and Figure 14. With respect to the $\mu - M$ and $\beta - M$ relations the materials tested fall in two groups; acetate, nylon 66, Fibravyl, and Terlenka on the one hand and cotton, viscose rayon, and Saran on the other. Both curves intersect at Teflon, which material shows the lowest μ, β, and M values.

It is evident that a relation between chemical structure and frictional behavior exists.

For wool also very low μ values have been found; according to Gralén [8] this effect must be ascribed to the low chemical reactivity of the outer layers of the fiber (the epicuticule).

A comparison of the stress–strain curves of different materials [29] shows that the cotton fiber possesses a low elasticity. It is a well-known fact that hydrogen bonding between the chain molecules of the cellulose is responsible for this behavior. Wool, on the other hand, is much more elastic in nature; according to Grosberg [9] the friction of wool is practically an elastic phenomenon.

TABLE XII. Values of the Molecular Cohesion Energy M, μ, and β for Various Materials

Material	M [6, 16, 21], cal./mole	μ_{300}	β_{300}	μ_{600}	β_{600}	
Cellulose	6200	0.331	0.645	0.327	0.643	Mean for cotton
		0.350	0.666	0.334	0.601	Mean for viscose
Cell. acetate	3800	0.467	0.855	0.432	0.628	Mean for acetate
Saran	3500	0.322	0.515	0.272	0.377	
Nylon 66	3400	0.459	0.814	0.436	0.840	
Fibravyl	2500	0.362	0.706	0.373	0.831	
Terlenka	1900	0.349	0.625	0.323	0.560	
Teflon	1600	0.273	0.466	0.239	0.352	

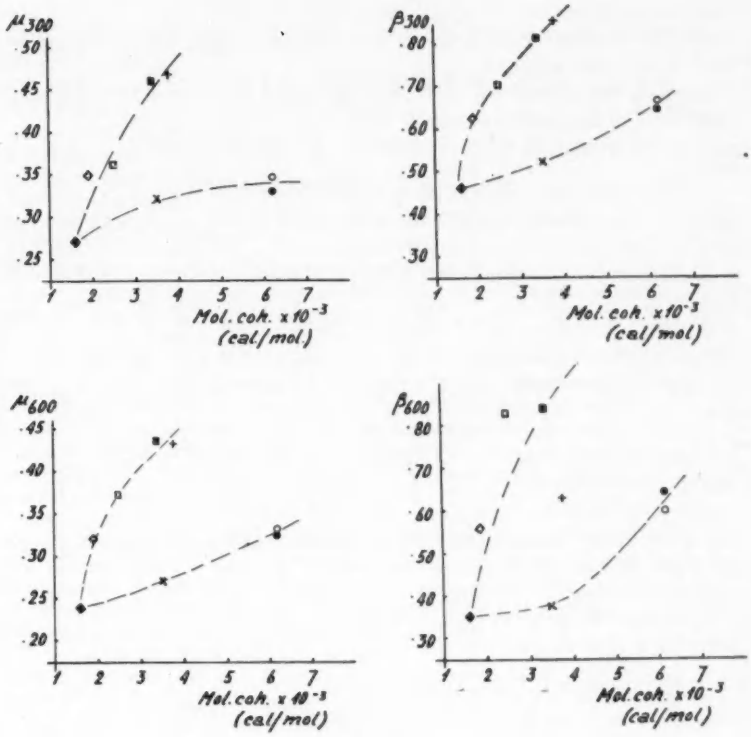

Fig. 14. Relation between the molecular cohesion and μ_{300}, μ_{600}, β_{300}, and β_{600}. ●: cotton, ○: viscose, +: acetate, ×: Saran, ■: nylon 66, □: Fibravyl, ◇: Terlenka, ◆: Teflon.

One would expect that fibers with a low elasticity possess a high μ value; in broad outlines this seems to be the case.

Viscose and acetate seem to behave differently; the μ values of viscose are practically the same as those of cotton, but the first fiber shows a much higher elasticity. The μ values of acetate rayon are even higher than those of cotton and viscose rayon.

For rayon this difference is only apparent, for the higher orientation of the cellulose molecules in the outer layers of the fiber certainly causes a much lower elasticity—comparable with that of the cotton fiber—than the mean value for the fiber as a whole. It is this outer layer that is of importance for our frictional measurements.

From this comparison of the elastic properties of viscose and cotton we must conclude that the frictional behavior of a synthetic fiber will be dependent on the amount of stretch applied when spinning the fiber.

Our measurements on high and low tenacity Enkalon indeed showed higher μ and β values for the first material. Also, the highly orientated nylon fiber possessed a high μ value.

Gralén [8] mentions some experiments carried out on terylene fiber by Carlene, by means of the twist friction meter described by Lindberg and Gralén. The Terylene fiber shows a circular cross section; by treating with 10% NaOH solution for different times of reaction these fibers were "peeled off" uniformly and concentrically. The diameter of the fibers, therefore, varied from 13.5 to 18.3 μ; from these measurements an increase of the coefficient of friction could be established with increasing diameter of the fiber. This peeling-off, however, eliminates the most strongly orientated parts of the fiber; in our opinion, therefore, the difference in degree of orientation between a normal and a peeled-off fiber is responsible for the different frictional behavior.

Differences in Frictional Behavior Within Cotton

In contradiction to the results of Lord, we could establish that for cotton the coefficient of static

friction is dependent only on the genesis of the fiber: *Gossypium barbadense* shows a lower μ value than *Gossypium hirsutum*.

Swelling the fiber in 18% NaOH decreased the coefficient of friction considerably, which phenomenon can be explained by three causes:

1. The fiber cross section after swelling is more circular than before, which diminishes the number of points of contact between the fibers.
2. The crystallinity of the fiber is decreased [22].
3. The crystal lattice is changed; the distance between the cellulose molecules is increased with a corresponding decrease of the molecular cohesion.

This decrease of μ is negatively correlated with the maturity of the fiber: a mature fiber swells less than an immature one.

At lower values of the normal load, this decreasing effect is not present; probably at these values the saponification of the cotton wax, being a specific surface phenomenon, is of paramount influence.

Scouring with diluted NaOH resulted in an increase of μ, caused by

a. the elimination of the cotton wax,
b. the recrystallization of the cellulose, as described by Nelson, Segal, and Ziifle [25].

Decrystallization of the cotton by treating with ethylamine increased the coefficient of friction, probably by the dewaxing of the fiber; at higher values the decreasing effect of the decrystallization seems to play its part.

Acknowledgment

The author is especially indebted to Mr. D. F. van de Riet for his assistance in the experimental work, to Miss Doraline Wabeke of the Mathematical Centre, Amsterdam, for her statistical contributions, to Dr. H. L. Röder (AKU, Arnhem), Ir. F. H. Germans (Stichting Onderlinge Research, Hengelo) and Dr. L. Segal (Southern Regional Research Laboratory, New Orleans) for supplying various fiber samples.

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Electric Network Analog Study of Viscous Flow Normal to Parallel, Evenly Spaced Cylinders

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Abstract

In connection with the study of viscous flow of liquids and gases between textile fibers, an electric resistance network analog was employed to solve the Navier-Stokes equations for creeping flow normal to an infinite array of circular cylinders arranged in a hexagonal pattern. The results of the analog study predict flow resistances approximately four times as great as those measured with real packages of fibers. The factor of four difference between predicted and experimentally measured resistances is very likely due to the uneven spacing of fibers in the real case, giving some very large passages which offer relatively little resistance to a significant fraction of the flow.

However, the variation of flow resistance with porosity appears the same, on a percentage basis, for the analog prediction based on equally spaced fibers as for the experimentally measured resistance of real fiber masses which are unequally spaced in a random fashion.

Thus neither the predicted nor measured flow resistance varies with fiber mass porosity in accordance with the Carmen-Kozeny formula which has been successfully applied to flows through granular beds; there is now little reason to believe that the large variation of the Kozeny "constant" with porosity of the fiber mass is due simply to shift of passage size distribution with degree of packing of the textile fibers.

Introduction

The work described in this paper, aimed at gaining a better understanding of flow of fluids past fibers in connection with wet processing of textile materials, grew out of research activity at the Swedish Institute for Textile Research in Gothenburg, Sweden. Early attempts to characterize the resistance to flow through various kinds of masses of textile fibers assumed that the characteristics of flow through fiber masses are similar to the characteristics of flow through granular beds, a subject which has been thoroughly studied in connection with ground water flow through various soils and in connection with various kinds of fluid filtration using beds of granular media. Although the pressure drop is linearly related to rate of flow in both cases, there seems to be a significant difference in the way in which resistance to flow varies with porosity in the case of flow through masses of fibers as compared with the flow through granular beds.

The significant difference between these two flow situations has been thoroughly delineated by Lord [6]; he has compiled the results of extensive data taken on the flow of air through fibrous masses, giving a thorough empirical analysis of the results. He shows that, whereas the flow of fluids through granular beds can be characterized by an equation containing a constant, sometimes called the Kozeny "constant," the corresponding quantity in an equation representing the flow through masses of fibers is not a constant but rather a quantity which varies considerably with porosity, especially in the regions of high porosity. In his paper, Lord also discusses the work by Emersleben [3] on flow parallel to evenly spaced cylinders (fibers); he shows, in this case, that one can expect a large variation of the so-called Kozeny constant with porosity in the ranges of high porosity. Limited experimental work carried out by the author at the Swedish Institute for Textile Research with the flow of water through approximately parallel-oriented nylon fibers in a direction normal to their axes of orientation established the applicability of Lord's empirical work on air flows to liquid flows as well.

Because of the very complicated nature of the precise flow paths between even carefully aligned fibers (as, for instance, in a yarn), it did not seem possible to describe these flow passages in any pre-

cise way, and it also seemed difficult to assess in any quantitative way the manner in which these flow passages changed with change in porosity. Thus, it was impossible to say whether the change in Kozeny constant with porosity was due to change in the size distribution of the flow passages or whether it was due to some basic fluid flow phenomena that would hold even if the fibers were all perfectly spaced. The desire to gain a better understanding of the flow through evenly spaced fibers in a direction normal to their parallel orientation direction was intensified by the fact that most arrangements of textile fibers that are encountered in wet processing are more or less parallel arrangements with the flow normal to the axes of the fibers as, for instance, in packed fibers, in package dyeing, in yarns, and in the dyeing of woven fabrics.

A thorough search of the literature in the field of fluid flow did not reveal an available solution to the problem of flow past circular cylinders that was hoped for, at least not for the case of an infinite array of circular cylinders. The work of Stokes [12] on the flow past a single sphere and a single cylinder and his difficulty with finding a solution for the case of viscous flow past a single cylinder, the work of Oseen [8] on the approximate solution for the viscous flow past a single cylinder, and the solution by Thom [13] for the flow past a single cylinder were, of course, found. However, the results of the work carried out by these men are not directly applicable to the flow past an array of many, many cylinders.

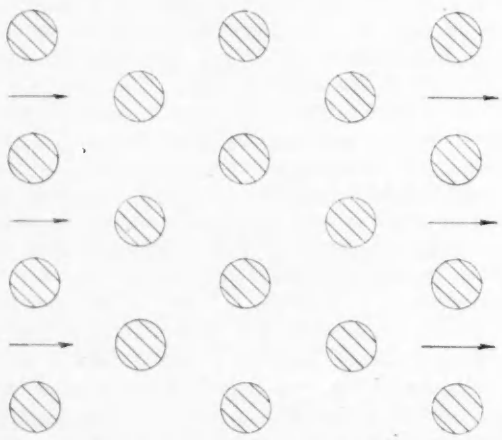

Fig. 1. Diagram showing flow direction relative to cylinders arranged in hexagonal pattern.

Statement of Problem

Although the specific pattern of spacing for the fibers may have some influence on the resistance to flow through them, the primary aim of this work was only to gain a qualitative understanding of the flow normal to large numbers of packed fibers. Thus it seemed worthwhile to begin by investigating a special case in which the fibers (cylinders) are perfectly parallel and uniformly spaced. Furthermore, it was decided to concentrate on fibers spaced in a hexagonal pattern with the normal flow direction as shown in Figure 1. By making full use of symmetry, one need only study the flow through a region shaped like that shown in Figure 2, since this shape is repeated over and over again in the field of flow, which is assumed to extend to infinity in all directions. Although there are chamber wall effects that may be important when relatively few fibers are contained in a correspondingly small chamber, these effects seem negligible in most practical problems encountered in the wet processing of textile materials. The methods of analysis employed here for this study could be applied, at the cost of considerable complexity and effort, to small groups of cylinders located between chamber walls.

Boundary Conditions

For the flow region or control volume shown in Figure 2, the boundary conditions may be deduced as follows. First, each of the circular portions of the boundary must have a constant stream function,[1] since no flow passes through them. Second, by considerations of symmetry, the upper and lower horizontal boundaries must have the same value of stream function as the circular boundary with which it connects. Thus the flow is bounded top and bottom by streamlines, each representing a unique value of stream function, the difference of which represents the rate of flow through the control volume. Third, the fluid velocity at the walls of the cylinders must be zero; otherwise an infinite shear stress would exist between the fluid and the cylinder walls. Thus the rate of change of stream function normal to the circular boundaries is zero. Fourth, it may be deduced from symmetry that the shear stresses in the fluid at the upper and lower horizontal boundaries are zero. Finally, symmetry also indicates that all the streamlines of the flow

[1] The stream function is constant along a streamline.

should be horizontal at the vertical boundaries of the control volume (i.e., as the fluid enters and leaves the control volume).

Basic Differential Equations

When both viscous forces and inertial forces in the fluid are important in a flow region such as this, the stream function ψ must satisfy the Navier-Stokes equation [11]

$$\partial(\Delta\psi)/\partial t + u\partial(\Delta\psi)/\partial x + v\partial(\Delta\psi)/\partial y = \frac{\mu}{\rho}\Delta\Delta\psi \quad (1)$$

where $\Delta\psi = \partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2$, $u = \partial\psi/\partial y = x$-component of fluid velocity, $v = -\partial\psi/\partial x = y$-component of fluid velocity, μ = absolute viscosity of fluid, ρ = mass density of fluid, and $\Delta\Delta\psi = \partial^4\psi/\partial x^4 + 2\partial^4\psi/\partial x^2\partial y^2 + \partial^4\psi/\partial y^4$. Since this is a steady flow problem, $\partial(\Delta\psi)/\partial t \equiv 0$. When the fluid velocity is everywhere very small, the flow is described as a creeping flow [11], and the quantities u and v may be so small as to be negligible. When this is so, Equation 1 then may be simplified for the case of steady flow to

$$\Delta\Delta\psi = 0 \quad (2)$$

Because the fluid velocities in this problem appear to be very small, it seems reasonable to proceed with Equation 2 and then check the validity of this assumption that the velocity terms may be neglected in Equation 1 after the solution to Equation 2 is at hand, giving estimates of $\partial(\Delta\psi)/\partial x$ and $\partial(\Delta\psi)/\partial y$.

The fluid pressure is also a significant variable in this problem (we need to know the difference in pressure between entrance and exit for the flow region shown in Figure 2 for a given rate of flow through the system); it is given by

$$\text{grad } p = \mu\Delta\vec{w} \quad (3)$$

or

$$\partial p/\partial x = \mu\partial(\Delta\psi)\partial y \quad (4)$$

and

$$\partial p/\partial y = -\mu\partial(\Delta\psi)\partial x \quad (5)$$

Thus it is seen that the pressure drop for the system may be obtained by integrating Equation 3 or Equations 4 and 5 between entrance and exit points after the stream function ψ has been determined.

The basic problem then is to determine ψ as a function of x and y for the boundary conditions

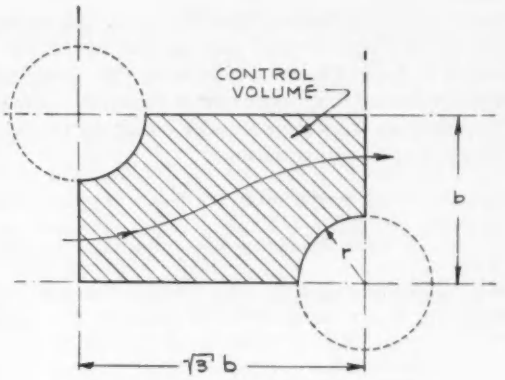

Fig. 2. Basic control volume to be studied.

enumerated above. This problem is similar in many respects to that of finding the stress function in problems of plane stress and plane strain in the field of elasticity, in that it is necessary to find a biharmonic function that will fit the boundary conditions. Because of the apparently insurmountable difficulty of finding a doubly periodic analytical solution for the stream function ψ, it was necessary to proceed to find an approximate solution based on a finite difference approximation to Equation 2. The finite difference approximation to Equation 2 [2, 14] is given by

$$\Delta^2\psi \approx [20\psi_0 - 8(\psi_1 + \psi_2 + \psi_3 + \psi_4) + 2(\psi_6 + \psi_8 + \psi_{10} + \psi_{12}) + \psi_5 + \psi_7 + \psi_9 + \psi_{11}]/\delta^4 = 0 \quad (6)$$

or by

$$\Delta^2\psi = \Delta F \approx (F_1 + F_2 + F_3 + F_4 - 4F_0)/\delta^2 \quad (7)$$

where

$$F = \Delta\psi \approx (\psi_1 + \psi_2 + \psi_3 + \psi_4 - 4\psi_0)/\delta^2 \quad (8)$$

where the numerical subscripts refer to the points of the grid shown in Figure 3. The advantages of employing the auxiliary function F defined above have been demonstrated by many workers [1, 10, 13] who have employed relaxation methods and many others [5, 9] who have employed resistance network analogs to obtain solutions of the biharmonic differential equation.

Description of Electric Network Analog Method

The electric analog study of this particular fluid flow problem employed a cascaded resistance network similar to the networks employed by Lieb-

mann [5] and Palmer and Redshaw [9]. However, instead of being divided into a network of horizontal and vertical rows of squares, the flow field was divided up into approximate "squares" formed by orthogonal functions ξ and η satisfying the harmonic (LaPlacian) equation

$$\Delta\xi = \partial^2\xi/\partial x^2 + \partial^2\xi/\partial y^2 = 0 \qquad (9)$$

$$\Delta\eta = \partial^2\eta/\partial x^2 + \partial^2\eta/\partial y^2 = 0 \qquad (10)$$

and coinciding regularly with the boundaries of the fluid flow region as shown in Figure 4. The lines of constant ξ and constant η were found by using teledeltos paper [4] as a resistance network analog [7]. It was found that, due to the random nonuniformity of the resistance of the graphite coating on the paper and the existence of troublesome contact resistance at the boundaries, it was difficult to get very precise results with teledeltos paper. However, the results were carefully examined for gross errors and an averaging procedure was employed to remove many of the smaller irregularities that were observed.

The problem was thus transformed from the x–y coordinates to the ξ–η coordinates, as suggested by Thom [13]. This transformation was made in order to simplify introduction of the boundary conditions and to minimize the number of network nodes required to obtain reasonably accurate results. A cascaded resistor network [5, 9] was then set up to solve the equations

$$\partial^2F/\partial\xi^2 + \partial^2F/\partial\eta^2 \approx (F_a + F_b + F_c + F_d - 4F_o)/\delta^2 \qquad (11)$$

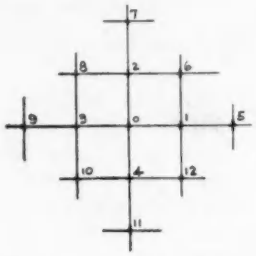

Fig. 3. Diagram of node points in a finite difference network.

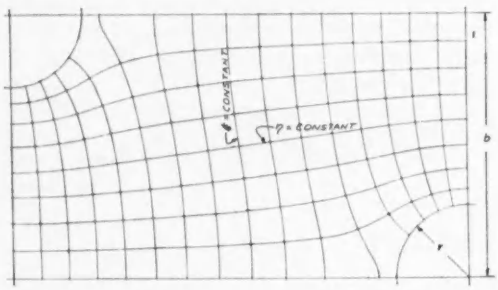

Fig. 4. Mapping of flow field with orthogonal functions ξ and η for the case $r/b = 0.275$.

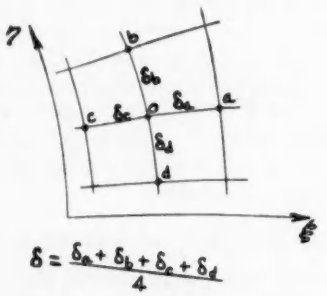

Fig. 5. Diagram showing arrangement of node points on ξ–η network.

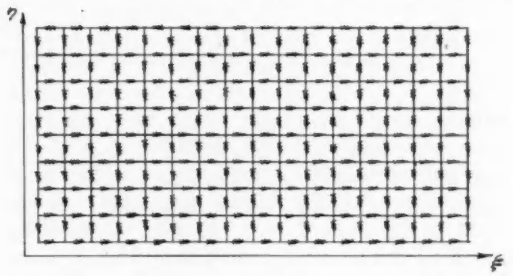

Fig. 6. Arrangement of resistors in the analog networks.

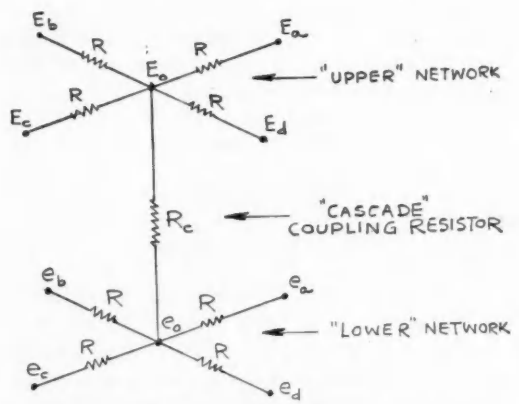

Fig. 7. Schematic arrangement of resistors to form cascaded networks.

and

$$F_0 = \partial^2\psi/\partial\xi^2 + \partial^2\psi/\partial\eta^2 \approx (\psi_a + \psi_b + \psi_c + \psi_d - 4\psi_o)/\delta^2 \quad (12)$$

where the letter subscripts refer to the points of the ξ–η grid about a node o as shown in Figure 5. The quantity δ is the average spacing of the network in the flow field at the node o and varies from node to node in the network in the flow field. However, the resistor networks were arranged in horizontal and vertical rows as shown in Figure 6, the lines of constant ξ and constant η forming a network of perfect squares. Figure 7 illustrates schematically the resistances associated with computing Equations 11 and 12. The "upper" and "lower" networks both employed 100-ohm precision ($\pm 0.5\%$) carbon resistors selected to give no more than 0.1% variation from one resistor to the next. The "cascade" resistors were precision carbon resistors combined in parallel to give required values to within $\pm 0.1\%$. The electric potentials at the nodes of the "upper" network represented the function $F = \Delta\psi$ and had a maximum value of 10 volts. The electric potentials at the nodes of the "lower" network represented the stream function ψ and had a maximum value of 0.02 volt. Thus the current flowing in each cascade resistor was very nearly independent of the "lower" network voltage acting on it. The analog equations corresponding to Equations 11 and 12 were then shown to equal

$$E_a + E_b + E_c + E_d = 4E_o \quad (13)$$

and

$$-E_o/R_c = (e_a + e_b + e_c + e_d - 4e_o)/R \quad (14)$$

It is now possible to set $-E = F$ and $e = \psi$, in which case $R/R_c = \delta^2$. Thus the cascade resistors R_c have varying values, depending on the local average value of δ: $R_c = R/\delta^2$.

Design Details

In designing the electric network, the decision was made to build the upper and lower networks in overlapping fashion under the terminal board on which they were mounted, as shown in Figure 8. Thus, it was possible to install the cascade resistances R_c on special holders that could be plugged onto the tops of the adjacent terminals at corresponding node points as shown in Figure 9. This made the necessary changing of the resistors R_c as simple as possible and also made all node points of both the upper and lower networks easily available for measuring electric potentials during the study. The resistance analog was built in a number of sections that could be connected at appropriate boundaries in "building block fashion" to carry out the various solutions requiring various numbers of rows of node points. Precision-selected 200-ohm

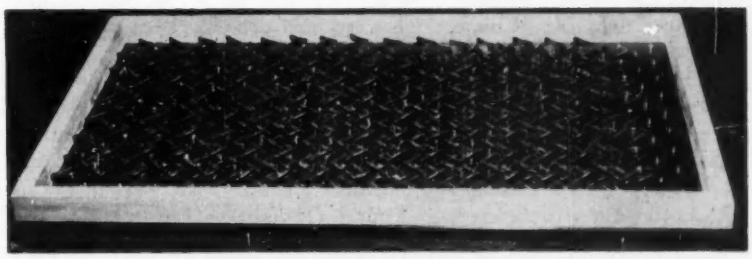

Fig. 8. Photograph of bottom side of terminal board showing overlapping construction of both the upper and lower resistance networks under the terminal board.

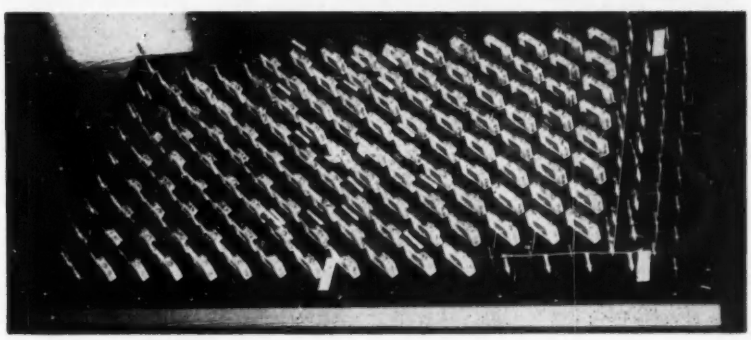

Fig. 9. Photograph of top side of terminal board showing cascade resistances mounted on special holders plugged to corresponding terminals of adjacent networks.

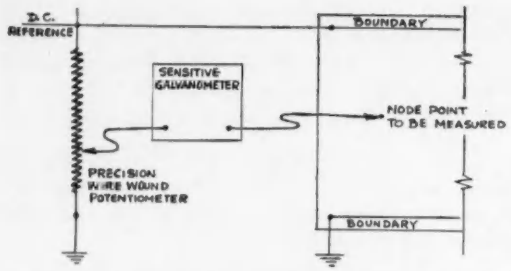

Fig. 10. Schematic diagram of null balance scheme to measure network node potentials.

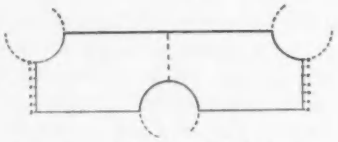

Fig. 11. Basic control volume which includes a complete cycle of flow pattern.

resistors, similar to the 100-ohm resistors mentioned earlier, were employed between points along all boundaries to be connected together.

In order to facilitate introduction of boundary conditions, additional units were constructed having wire-wound potentiometers to adjust the voltage drop between a storage battery supply (+12v. and −12v.) and individual boundary node points of the upper network. Connections were also provided through these units to facilitate reading the potentials on the first three rows of node points of the lower network to satisfy the boundary condition of zero gradient of ψ normal to the cylinders.

A very sensitive rotating-mirror galvanometer[2] was employed as a null voltage indicator together with a ten-turn precision wire-wound (Helipot) potentiometer to measure the network potentials as shown in Figure 10.

Discussion of Analog Study

Because of the final condition of symmetry expressed earlier in the statement of boundary conditions, it was found unnecessary to set any conditions along the network boundaries corresponding to the vertical boundaries of the control volume shown in Figure 2. To prove this, a coarse network was connected to study the flow through the control volume shown in Figure 11. In this case, it was possible to connect corresponding right-end and left-end node points of the resistance networks (indicated by ×-marks) by good conductors, because this control volume represents a complete cycle of flow, and the stream function and all of its derivatives must have identical values at corresponding points along the two vertical boundaries. This auxiliary study proved the symmetry condition, because it gave the same results as were found by studying the flow field enclosed by the control volume shown in Figure 2 and letting the nodes of both the ψ and F networks seek their own values. In both cases the streamlines were found to be horizontal at the vertical boundaries of the control volumes.

In order to satisfy the conditions relating to the value of the stream function itself along the upper and lower boundaries, all the points along the lower boundary of the ψ network of the electric analog were connected together and subjected to a potential of −.0187 volt and all the points along the upper boundary of the ψ network were connected together and subjected to a potential of +.0187 volt. To satisfy the condition of zero shear stress along the horizontal parts of the upper and lower boundaries of Figure 2, the shear stress at a given point of the flow field is given by

$$\tau_{xy} = \mu(\partial^2\psi/\partial y^2 - \partial^2\psi/\partial x^2) \qquad (15)$$

Since ψ does not vary with x along this portion of the boundary, $\partial^2\psi/\partial x^2 = 0$. Thus, since $\tau_{xy} = \partial^2\psi/\partial x^2 = 0$ along this boundary, $\partial^2\psi/\partial y^2 = 0$ and we may also write $F = \partial^2\psi/\partial y^2 + \partial^2\psi/\partial x^2 = 0$ along this part of the boundary. To satisfy this condition on the electric analog, all the node points of the E network along the upper and lower boundaries corresponding to the horizontal parts of the upper and lower boundaries of Figure 2 were connected together and subjected to zero (ground) potential. The condition of zero rate of change of stream function normal to the cylinder walls was satisfied on the electric analog by adjusting the potentials of the remaining node points on the upper and lower boundaries of the E network until the potentials of the first three node points on each vertical line inward from these portions of the boundary of the e network lay on a parabolic curve when plotted as a function of distance from the boundary (i.e.,

[2] In this case, we used a Multiflex Galvanometer, manufactured by Hugo Tillquist, Stockholm, having an input impedance of 5000 ohms and resolution of about 2×10^{-9} amperes.

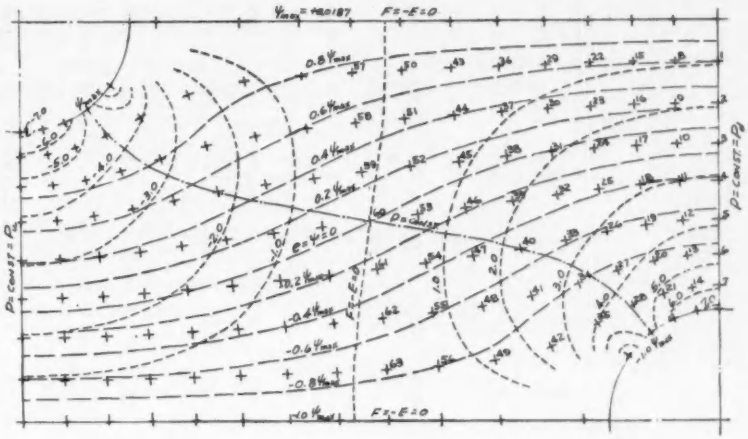

Fig. 12. Resistance network analog solution represented on the actual flow field (x–y coordinates) for the case $r/b = 0.275$. Direction of flow is from left to right.

the difference between the boundary node point potential and the node point potential on the second row was one third of the difference between the node point potentials of the second and third rows). This process of adjusting the voltages along the boundary of the E network to satisfy the gradient condition on the e network was a form of relaxation or trial and error technique and required some patience and care in its execution.

The results of a typical electric analog study are shown in Table I and Figure 12. The data shown in Table I were recorded directly from readings taken of node potentials of both networks on the electric analog. These data have been transferred to the actual flow field in Figure 12, and streamlines (lines of constant ψ) and lines of constant F have been approximated by linear interpolation of the data shown in Table I.

The pressure drop between the left and right ends of the flow field may be calculated by approximately integrating Equations 4 and 5 through the summation of appropriate differences of potential occurring on the electric analog. In other words,

$$\partial p/\partial x = \mu\partial(\Delta\psi)/\partial y = \mu\partial F/\partial y = -\mu\partial E/\partial y \quad (16)$$

or

$$\partial p/\partial \xi = -\mu\partial E/\partial \eta \quad (17)$$

Integrating,

$$P_b - P_a = -\mu \int_{\xi_a}^{\xi_b} (\partial E/\partial \eta)\, d\xi \Big|_{\eta=\text{const.}}$$

$$\approx -\mu \sum_{a}^{b} (E_{\text{diff.}}/\eta_{\text{diff.}})\xi_{\text{diff.}} \Big|_{\eta=\text{const.}} \quad (18)$$

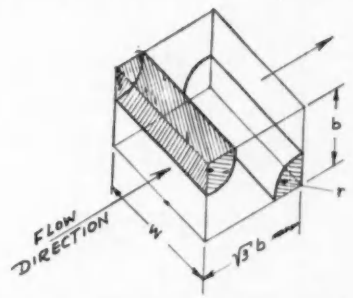

Fig. 13. Control volume for computation of Kozeny constant from analog results.

From Table I and Figure 12, noting that $\xi_{\text{diff.}} = \eta_{\text{diff.}}$

$$P_u - P_d \approx -\mu \sum_{d}^{u} E_{\text{diff.}} \Big|_{\eta=\text{const.}}$$

$$\approx \mu \begin{Bmatrix} (E_3 - E_5)/2 + E_{10} - E_{12} + E_{17} - E_{19} \\ + E_{24} - E_{26} + E_{31} - E_{33} + E_{38} - E_{40} \\ + E_{45} - E_{47} + E_{52} - E_{54} + (E_{59} - E_{61})/2 \end{Bmatrix} \quad (19)$$

By way of completeness, it is worth noting that lines of constant pressure are orthogonal to the lines of constant E and F. Thus a line representing a pressure halfway between the upstream pressure P_u and the downstream pressure P_d would look something like that sketched in Figure 12 through the center of the flow field.

Discussion of Results

Electric network analog solutions were obtained for four different cylinder diameter-to-cylinder spacing ratios corresponding to porosities ranging from 0.715 to 0.958. In all cases, the F function was

TABLE I. Data Taken from Resistance Network Analog Study for the Case $r/b = 0.275$*

Potential E	639	575	554	368	588	0	0	0	0	0	0	0	0	0	0	0	0
Node point No.	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Potential e	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
E	482	460	423	349	325	131	059	027	009	−004	−014	−022	−030	−037	−042	−045	−048
No.	113	106	99	92	85	78	71	64	57	50	43	36	29	22	15	8	1
e	963	963	962	958	950	910	854	804	762	726	696	670	648	632	621	615	612
E	370	358	329	282	231	141	078	038	011	−010	−028	−045	−061	−075	−086	−092	− 95
No.	114	107	100	93	86	79	72	65	58	51	44	37	30	23	16	9	2
e	855	855	847	826	797	739	664	588	517	455	399	350	310	280	259	246	243
E	282	274	253	219	176	122	075	038	007	−019	−044	−070	−095	−116	−133	−144	−148
No.	115	108	101	94	87	80	73	66	59	52	45	38	31	24	17	10	3
e	666	662	649	622	579	514	435	349	263	183	107	040	−012	−053	−081	−097	−102
E	210	205	189	165	133	097	062	030	0	−029	−060	−095	−132	−163	−187	−203	−209
No.	116	109	102	95	88	81	74	67	60	53	46	39	32	25	18	11	4
e	412	406	391	361	316	253	176	090	0	−086	−173	−253	−315	−362	−393	−409	−413
E	149	145	134	118	096	071	045	020	−007	−037	−073	−120	−173	−216	−250	−272	−280
No.	117	110	103	96	89	82	75	68	61	54	47	40	33	26	19	12	5
e	104	099	083	056	015	−036	−103	−179	−262	−347	−435	−515	−581	−624	−652	−666	−669
E	095	093	086	076	062	046	029	011	−010	−037	−076	−137	−226	−278	−326	−357	−369
No.	118	111	104	97	90	83	76	69	62	55	48	41	34	27	20	13	6
e	−242	−247	−258	−279	−310	−350	−400	−455	−519	−589	−665	−740	−799	−828	−850	−859	−858
E	047	046	042	037	031	023	014	004	−008	−025	−057	−128	−317	−345	−418	−460	−480
No.	119	112	105	98	91	84	77	70	63	56	49	42	35	28	21	14	7
e	−616	−617	−624	−635	−651	−672	−698	−728	−764	−806	−855	−911	−951	−959	−964	−967	−967
E	0	0	0	0	0	0	0	0	0	0	0	0	−567	−366	−540	−584	−632
No.	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
e	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000	−1000

* On the upper network, the number 1000 represents a potential E of 10 volts; on the lower network, the number 1000 represents a potential e of 0.0187 volts.

found to have a second peak magnitude along the circular boundary near the horizontal boundary. However, there is considerable uncertainty about this second peak value because of the relatively coarse network employed and the presence of a singularity at the point where the circular boundary meets the straight boundary.

The results of the above four electric analog studies were used to compute the Kozeny constant and determine how it is affected by porosity. The Carmen-Kozeny equation [6] gives the following relationship between pressure drop and rate of flow for a porous medium:

$$Q/(P_u - P_d) = (1/K)(A/S_0^2\mu L)[\epsilon^3/(1-\epsilon)^2] \quad (20)$$

where Q = volume rate of flow (L^3/T), $(P_u - P_d)$ = pressure drop in flow direction (F/L^3), K = Kozeny constant, A = total area normal to flow (L^2), S_0 = total surface of particles ÷ total volume of particles $(1/L)$, μ = fluid viscosity (FT/L^2), L = distance between P_u and P_d (L), and ϵ = porosity = (total volume − particle volume) ÷ total volume. For the case of flow past uniformly (hexagonally) spaced cylinders normal to their axes as shown in Figure 13, we obtain

$$Q/(P_u - P_d) = (1/K)(wba^2/4\mu\sqrt{3}b)[\epsilon^3/(1-\epsilon)^2] \quad (21)$$

where $\epsilon = 1 - (\pi a^2/2\sqrt{3}b^2)$. Relating this to the electric analog results, where $Q = 2w\psi_{\max} = 2we_{\max}$ and $(P_u - P_d) \approx -\mu \sum_d^u E_{\text{diff.}}|_{\psi=\text{const.}}$ we may solve for K

$$K \approx \left(-\mu \sum_d^u E_{\text{diff.}}/2we_{\max}\right) \times (wb^2/4\sqrt{3}\mu)(a/b)^2[\epsilon^3/(1-\epsilon)^2] \quad (22)$$

We may also note that $R/R_c = \delta^2$. In this case $R/R_c = 100/50{,}000 = 1/500$ when $\delta = b/8$, so that $b^2 = 64/500 = 0.128$, giving

$$K = \left[\frac{-\sum_d^u E_{\text{diff.}}}{2e_{\max}}\right]\left[\frac{16}{500\sqrt{3}}\right]\left[\frac{a}{b}\right]^2 \times \left\{\frac{\left[1 - \frac{\pi}{2\sqrt{3}}\left[\frac{a}{b}\right]^2\right]^3}{\left[\frac{\pi}{2\sqrt{3}}\left[\frac{a}{b}\right]^2\right]^2}\right\} \quad (23)$$

The Kozeny constant K, calculated as indicated in Equation 23 from the analog data, is shown as a function of porosity ϵ in Figure 14. Also shown is a shaded area which includes the values of the Kozeny constant published by Lord [6] to demonstrate the variation of K with ϵ found from a great deal of experimental work with air flowing through textile fiber packages. A small amount of experimental work by the author on flow of water through packages of nylon fiber also gave values of K falling in this shaded band. It is interesting to note that the approximate mathematical analysis by Emersleben [3] for flow parallel to equally spaced fibers gives values of K which fall in this shaded area.

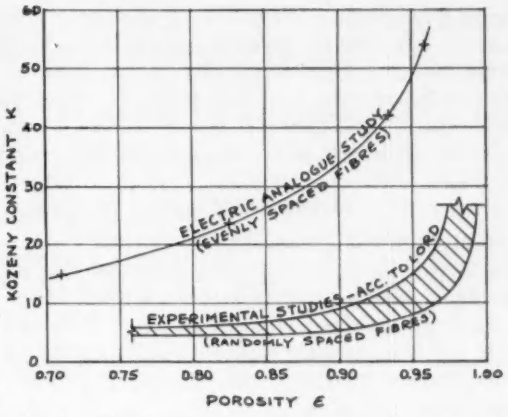

Fig. 14. Graphical representation of results of analog study compared to results of Lord's empirical analysis of experimental data.

Conclusions

From these results, it is evident that the resistance to flow through real packages of fibers is only about one fourth that which would be obtained if the fibers were uniformly spaced, but that the Kozeny constant seems to vary with porosity in approximately the same way (reckoned on a percentage basis) in both cases. Thus it is not likely that the variation with porosity in the real case can be explained by shift of passage size distribution with porosity (degree of packing). The factor-of-four difference between the experimentally derived values of K and those found from the analog study on the other hand are possibly due to uneven spacing of the fibers in the real case, giving some large passages which offer relatively little resistance to a large fraction of the total flow.

Subsequent work by Kärrholm ("A Flow Problem Solved by Strip Method," by Gunnar Kärr-

holm, *Transactions of Chalmers University of Technology*, Elanders Boktryckeri Aktiebolag, Gothenburg, Sweden, 1958) employing an analytical approach based on a "strip method" of solving the biharmonic equations gives results that are in substantial agreement with the results of this analog study.

Acknowledgments

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Interpretation of Fiber Properties

Part I: The Role of Single Fiber Flex Fatigue in Abrasion Resistance of Fabrics

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Abstract

The resistance of fibers to fracture due to fatigue in flexure is shown to correlate with the wear life of socks and can be used to explain other fabric abrasion resistance phenomena.

When single fibers are flexed over a rounded metal bar, the log of the number of flexures to failure has been found to be approximately linearly related to the radius of curvature of the surface of the bar and to the tension on the fiber during the test. An empirical equation is presented relating these variables along with some of the determined values for the various proportionality constants for several common fiber types.

The relative resistances of different types of fiber to scraping and grinding actions of emery particles was measured and compared with the generally accepted abrasion resistance of fabrics of these fibers. The correlation was so poor as to indicate only a slight probability that the grinding mechanism plays an important role in normal fabric abrasion.

THE factors contributing to fabric abrasion are not sufficiently well described in the literature to allow one to characterize and evaluate the single fiber properties involved. As pointed out by Backer [1], the mechanism of fabric abrasion differs from the process of surface attrition of solid bodies because of the complex geometry of fabric surfaces and the visco-elastic properties of textile fiber. It can be divided into three elements, the relative magnitude of each depending on the nature of the abradant, the behavior of the fiber in the fabric structure, and the general conditions of rubbing. These are friction, surface cutting, and fiber plucking.

Friction and surface cutting cover direct damage to the fiber at local points of contact with abrasive particles. Fiber plucking and other processes which produce fiber strains can cause immediate or dynamic-fatigue rupture of the fiber in tension or blending.

An attempt has been made to separate and evaluate the effect on the fibers of each of the components of the proposed mechanism of abrasion. This was done by comparing the resistance of different types of fibers to each component. The relative resistance of the fibers was then compared with the known durability of textiles made from them.

To measure the resistance of fibers to longitudinal gouging and scraping by hard protuberances, a method very similar to one described by Gonsalves [3] was employed. The principles are illustrated schematically in Figure 1. This depicts the manner in which single fibers were ground down by a specially treated, constant speed rotating emery wheel. The fibers were moved up and down at a constant speed while the emery wheel was oscillated back and forth, removing a nearly uniform amount of material over a long section of the fiber. After the grinding treatment, the samples were removed and the center portions were tested vibroscopically for denier loss.

In Table I, the various fibers are compared on the basis of the weight loss after the indicated arbitrarily chosen standard amount of treatment. Aside from the indication that nylon and polyester fibers are definitely superior, the test fails to discern a significant difference among such fibers as acetate, regenerated protein, and acrylics. These, of course, show considerable difference in resistance to wear in most applications. The high weight loss value for wool does not correlate with its generally good durability. Little difference was observed when the wheel was rotated so as to rub with scales rather

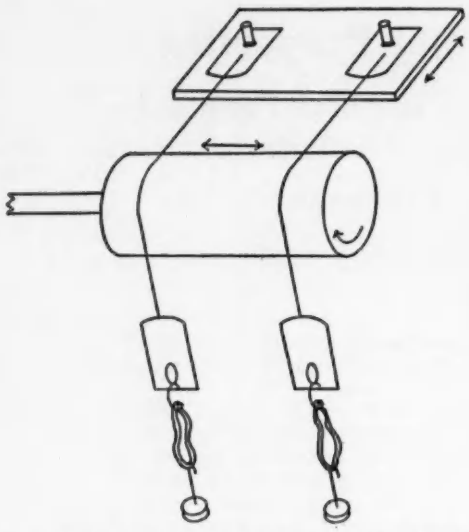

Fig. 1. Single fiber longitudinal abrader; abrasive wheel assembly.

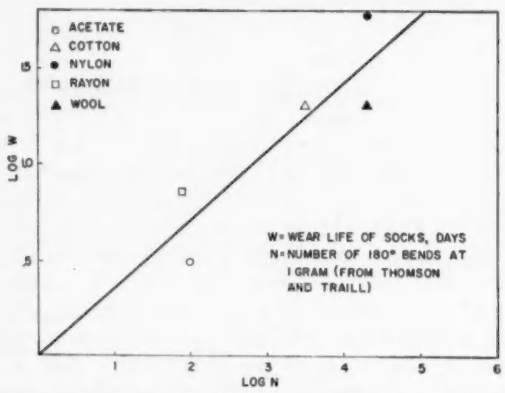

Fig. 2. Single fiber flex fatigue; correlation with wear tests.

than against them. In general, the agreement of the test with the known abrasion resistance of most apparel fabrics is poor.

To investigate the abrasive actions resulting from forces which are more of the nature of those produced by friction rather than by gouging or surface cutting, the emery wheel was replaced in the grinding apparatus by a rod covered with fibers which were combed out straight and laid down parallel to the axis of the rod. Thus, the test fiber was rubbed, as the rod was turned, by similar fibers which were fastened perpendicular to it.

Since there was no measurable wear in a 3-den. acrylic alloy fiber under the test conditions employed with the emery wheel, the up and down motion of the fiber was stopped and it was held so that it was rubbed in one spot. A tensioning weight of 1 g. was used which gave an actual total pressure of 1.4 g. between the test fiber and the ones on the mandrel. Under these conditions, the fibers rubbed approximately 50 miles over those on the mandrel without any detectable decrease in denier. These results are also given in Table I.

TABLE I. Effect of Longitudinal Grinding of Fibers

Fiber	Loss in denier	
	Emery wheel*	Fiber covered cylinders†
Nylon	0.05	—
Polyester	0.05	—
Acrylic	0.39	0
Zefran	0.40	0
Acetate	0.42	—
Regenerated protein	0.45	—
Wool	0.83	—

* w = 0.74 g.; t = 13.6 sec.; med-fine emery stone, turning 100 r.p.m.
† w = 1 g.; t = 24 hr.; r = 1800 r.p.m.

Fatigue in tension has been studied by many investigators. Comparable data are not available on a wide enough selection of fibers to allow for good comparative evaluations. In all cases, very severe conditions of stress or strain were required to produce failure in a reasonable amount of time. These conditions are so severe that it is difficult to envision their occurrence in "normal" fabric wear.

Thomson and Traill [4] studied fatigue resistance of fibers in bending. They repeatedly bent single fibers over rounded clamp ends under a load of 1 g. and recorded the number of 180° bends to break. Some of their results are compared in Figure 2 with the wear life of socks made from similar fibers as reported by Schiefer et al. [5]. The data are plotted as the log of the reported values for better comparison. The agreement as indicated is fair; it is good enough to suggest a correlation between bend fatigue and wear life. Dillon [2] has pointed out that the diameter of the fiber was a factor which was not considered by Thomson and Traill.

A modification of Thomson and Traill's test procedure was used; the apparatus is depicted schematically in Figure 3. The rod over which the fibers are pulled back and forth is a carboloy-tipped bar of

the type used in the Stoll Flex-Abrasion fabric tester. Microscopic examination of its edges indicated that the corners had a radius of curvature of 0.0009 in., which is over twice that of the circular cross section of a 3-den. polyacrylonitrile fiber. The rounded surface does not scrape an appreciable amount of material off the surface of the fibers, for while the fibers elongate or "grow" as a result of the repeated flexing under load, they do not lose weight. The test is normally run with the bar lubricated by machine oil. In general, lubricants appear to have little effect on the relative results.

The conditioned samples are prepared for flex test by measuring the denier of ten single fibers, attaching a standard size weight to each, and mounting them on the single fiber flex tester. No special selection or combination is necessary other than to make sure that the applied stresses cover a wide range. After a number of fibers have broken, the machine is stopped and they are replaced by other samples. The number of cycles to break each of the previous samples is recorded before resetting the counter and continuing the test. The data taken on a large number of nylon and acetate fibers are shown in Figure 4.

The data on nylon and acetate are typical though perhaps less scattered than those obtained on most fiber types. For these and all other types of fibers tested, the best fit seemed to be a straight line when log N is plotted vs. g./μ. The diameter was calculated from the denier and density of the fiber, assuming a circular cross section. In judging the scatter, one should note that each point represents only one single fiber test on fibers of various deniers. Use the nylon for example; most of the tests were run without special selection on staple filaments taken from a batch of nominal 3-den. fiber. However, some of the data represents 6-den. nylon.

Figure 5 shows a plot of the linear regression lines obtained from flex fatigue data taken on a variety of fibers. The correlation coefficients and constants are shown in Table II.

The values of log N at 0.04 g./μ are compared with the log of the number of days of sock wear life, as reported by Schiefer et al. [5], in Figure 6.[1]

The relatively short average wear life of socks as compared to other apparel would indicate that the damaging forces are quite severe in this application. Therefore, one would expect that the correlation of the log of the number of cycles to fracture with days of sock life should be best in a region of higher force. The difference in slopes of the lines in Figure 5 would indicate a different situation in the less severe

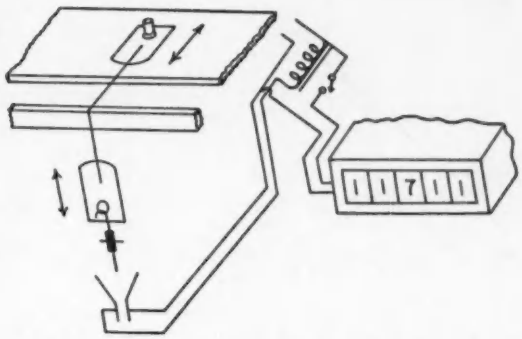

Fig. 3. Single fiber flex fatigue; flex bar assembly.

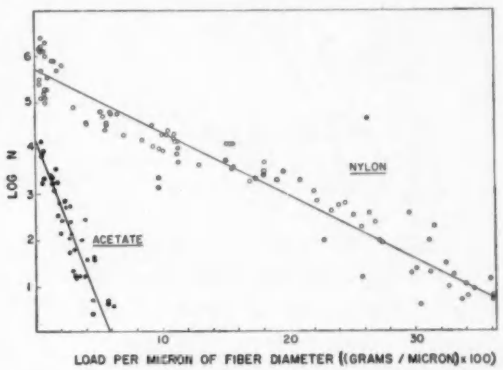

Fig. 4. Single fiber flex fatigue; log number of cycles to fracture vs. load per fiber diameter.

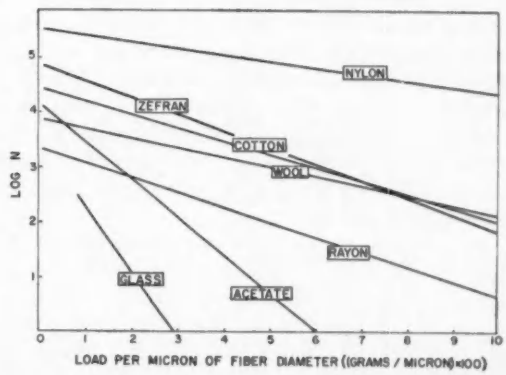

Fig. 5. Single fiber flex fatigue; behavior of various fibers.

[1] Other rayon samples with higher values have since been tested. This particular set was selected as being most probably indicative of rayons at the time the wear test was performed.

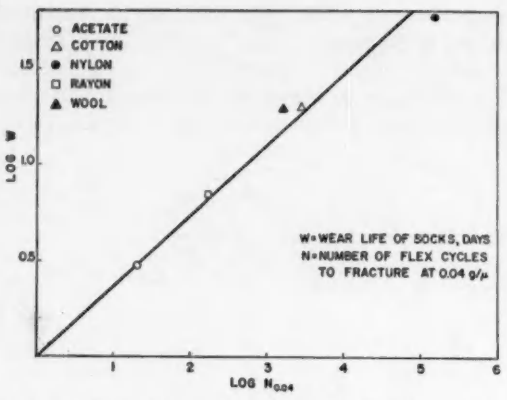

Fig. 6. Single fiber flex fatigue; correlation with wear life of socks.

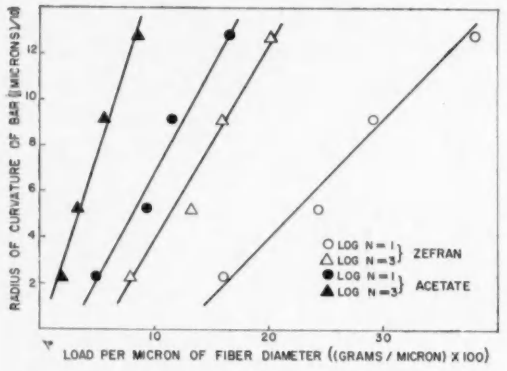
RADIUS OF CURVATURE OF BAR (MICRONS) √R
LOG N=1 ZEFRAN
LOG N=3 ZEFRAN
LOG N=1 ACETATE
LOG N=3 ACETATE
LOAD PER MICRON OF FIBER DIAMETER ((GRAMS / MICRON) X 100)

Fig. 7. Effect of radius of curvature of the flex bar.

applications and could account for some of the changes in relative abrasion resistances of different materials when service conditions are varied. There is little published data available on wear tests of various fibers under conditions involving lighter force applications. For cases where the effects of degrading influences, such as chemical or biological attacks or exposure to radiant energy, have been kept at a minimum, the relative values of the log of the number of flex cycles would appear to qualitatively fit known behavior of fabrics of the indicated fiber under these conditions.

The severity of the effect of the flex test on the fiber can be reduced by decreasing the weight attached to it or by increasing the radius of curvature of the bar. Figure 7 shows the latter effect on acetate and Zefran.[2] Again, we get what appears to

[2] Dow Chemical Company trademark.

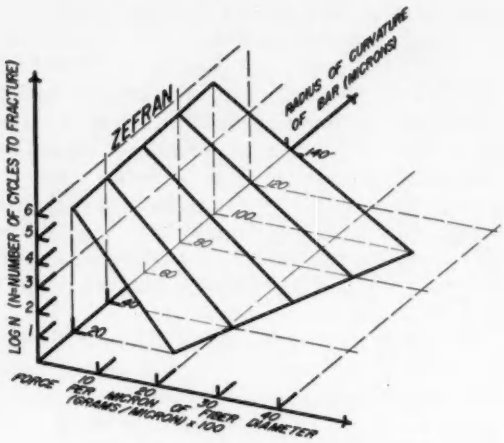
ZEFRAN
RADIUS OF CURVATURE OF BAR (MICRONS)
LOG N (N=NUMBER OF CYCLES TO FRACTURE)
FORCE PER MICRON OF FIBER DIAMETER (GRAMS / MICRON) x 100

Fig. 8. Single fiber flex fatigue.

be an approximately linear relationship for each bar of log N to the force per micron diameter. This indicates that the weight per micron of diameter required to fracture a fiber in any given number of cycles is nearly proportional to the radius of curvature of the bar over which it is flexed.

A diametric plot of the three variables is shown in Figure 8. This approximates a ruled surface of the second order and is a twisted plane. The twist is slight in the range of forces normally encountered in fabric wear and is due to the nonlinear relationship of log N and R at constant weight per micron of diameter.

The equation relating the three variables is given in Table II. Until more wear-life data are available under conditions involving different severity of application, the simple equation should represent the single fiber data with a sufficient degree of accuracy for most purposes.

For purposes of study of the internal mechanism leading to failure, it would be desirable to have an equation relating the various local stresses and strains to the experimental variables in the equation in Table II. The complexities imposed by the method of test have defeated preliminary attempts at analysis. The wide range of weights applied appear, through the microscope, to give all degrees of conformation of the fiber to the curved section of the bar from a close fit to contact at only one point. The difficulties of analyzing the effect of the variables over such a wide range of conditions suggest that it may be necessary to employ another type of

TABLE II. Single Fiber Flex Fatigue

$$\text{Log N} = -\frac{K_1R + K_2\frac{W}{D}}{K_3R + K_4\frac{W}{D}} + K_1R + K_2$$

Fiber	α/β*	α	γ	K_1	K_2	K_3	K_4
Zefran	29 (±4)	5.1 (±.2)	.94	0.0038	4.97	0.00194	0.130
Acetate	61 (±6)	4.1 (±.2)	.90	0.0096	3.86	0.00115	0.041
Wool	18 (±3)	3.9 (±.2)	.88	0.0019	3.89	0.00118	0.194
Rayon	25 (±4)	3.2 (±.1)	.89	0.0301	2.52	0.00182	0.088
Cotton	25 (±5)	4.5 (±.2)	.78				
Nylon	14 (±1)	5.7 (±.1)	.96				

*$\alpha = K_1R + K_2$ at R 22.6; $\beta = K_3R + K_4$ at R 22.6; γ = correlation coefficient.

experimental technique in which better control of the variables can be maintained.

Some of the variables other than radius of curvature of the bar have been studied. The effect of speed of the machine is small in the range of 1–100 cycles/min. The effect of stroke length on log N appears to be about the same as the effect of gauge length on tenacities. At zero length of stroke, as when the fiber is held in a clamp and bent in the same spot, as was done by Thomson and Traill, similar results are obtained (Figure 9). It is also interesting to note that their bend life data reported on cotton and viscose under different loads fits a straight line on a log N versus grams per micron of diameter plot with a fair degree of accuracy, as shown in Figure 10.

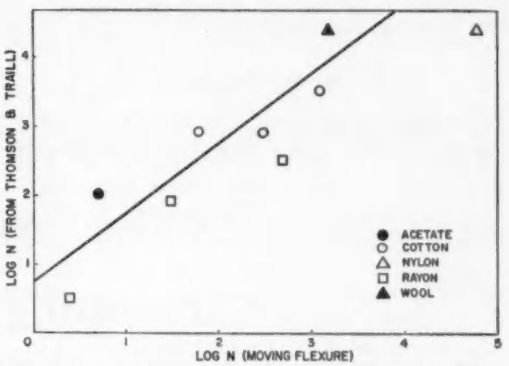

Fig. 9. Single fiber flex fatigue; correlation of localized bending with moving flexure at same wt./μ of diam.

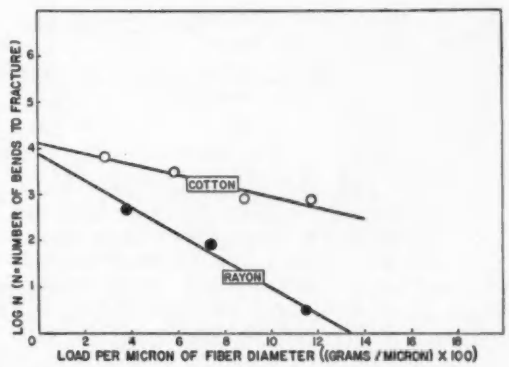

Fig. 10. Single fiber bend fatigue data from Thomson and Traill.

Summary and Conclusions

An investigation has been made of the resistance of single fibers to attrition by various types of physical processes. These processes were chosen because they were believed to be the most severe of those to which the fibers were subjected during the most common types of apparel wear. For widely different types of fiber, only one of these processes, the rate of fracture, caused by fatigue on repeated bending of single fibers, had any significant degree of correlation with the rate of their destruction in fabrics during actual wear tests.

The relative resistance of the fiber types to fatigue varies with the severity of the bending process. This behavior can explain the often observed phenomena of wide variations in the wear life of similarly constructed fabrics made from different fibers when they are subjected to different types of service conditions. It also can explain the lack of correlation of any single fabric abrasion test with actual performance in all but a narrow field of application.

A relatively simple test was developed to measure the resistance of single fibers to fatigue in flexure. By analysis of some of the variables in the test conditions, an empirical equation was developed which linearly relates, with a fair degree of accuracy, the log of the number of flex cycles to fracture to the

force per micron of diameter and to the radius of curvature of the bar over which the fiber is bent.

It must be recognized that the factors which influence the abrasion resistance of a fabric are numerous and complex. They vary greatly in relative importance depending on the type of external conditions to which it is subjected and to the actual structure and history of the fabric itself. The results of the study presented here would seem to indicate that the predominating mechanism of attrition due to rubbing and other physical processes in many if not most apparel applications is that of fracture of the fibers due to fatigue in flexure.

Acknowledgment

The authors are greatly indebted to Dr. R. A. Crane and Mr. P. C. Wharff for designing and building the instruments used in this work, to Mrs. Lola Parsons for competent operational assistance, and to the Dow Chemical Company for permission to publish this paper.

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Carbonizing Investigations

Part VI: A Comparison of Different Types of Surface Active Agents in Laboratory Carbonizing

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Abstract

Eighty-eight nonionic surface active agents, all containing polyoxyethylene as the hydrophilic group, and some anionic and cationic agents have been tested in the laboratory to determine the extent to which they protect wool from loss of tensile strength during carbonizing. Nonionic agents in which the lipophilic portion consists of polyoxypropylene provided little protection even at the highest concentrations tested, whereas nonionic agents containing an alkyl or aryl hydrocarbon group were generally effective. With the latter compounds, the length of the polyoxyethylene group influenced the optimal concentration of the reagent. Anionic agents were ineffective at low concentrations; cationic agents were comparable in their effects with nonionic agents.

Introduction

It has been shown [2] that the loss of tensile strength which occurs when wool is moistened with dilute sulfuric acid and baked at about 100° C. is decreased by the addition of surface active agents to the acid. The initial laboratory tests have been extended to industrial carbonizing trials [3] in which the inclusion of a nonionic surface active agent results in an increase in wool yield and the production of stronger yarn. In industrial practice the nonionic agent proved more effective than an anionic agent.

Laboratory experiments have now been made with

TABLE I. Mean Strength Ratings of Wool Carbonized in Sulfuric Acid Containing Various Types of Surface Active Agents

Type and number of surface active agent	Mean strength ratings (variance in parentheses)			
	0.001% S.A.A.*	0.003% S.A.A.	0.01% S.A.A.	0.03% S.A.A.
P.O.E.* esters of oleic, lauric, or stearic acids (16)	6.3 (3.3)	7.7 (2.4)	8.1 (1.1)	8.6 (1.5)
P.O.E. ethers of alkyl aryl hydrocarbons (29)	5.0 (5.4)	7.0 (3.8)	8.6 (0.9)	8.6 (1.0)
P.O.E. ethers of alkyl hydrocarbons (8)	6.5 (5.1)	8.1 (1.6)	8.4 (0.6)	8.6 (1.1)
Condensates of P.O.E. and P.O.P.* (7)	3.1 (1.1)	3.4 (0.3)	2.9 (0.5)	3.7 (4.3)
Condensates of P.O.E. and P.O.P. with ethylene diamine (9)	3.0 (1.0)	3.0 (0.5)	2.8 (0.4)	2.8 (1.7)
Anionic (8)	1.0 (0.0)	1.8 (1.1)	3.0 (6.6)	4.4 (9.4)
Cationic (5)	2.6 (2.8)	7.4 (4.8)	8.4 (0.3)	8.2 (0.7)
No surface active agent	2.4 (0.6)			
Untreated wool samples	9.2 (0.7)			

* S.A.A. = surface active agent; P.O.E. = polyoxyethylene; P.O.P. = polyoxypropylene.

88 commercially available nonionic surface active agents to compare their effectiveness for this purpose. For comparative purposes, several anionic and cationic agents have also been tested.

Materials and Methods

The Corriedale 56's wool and the method of acid impregnation, baking, and final neutralization were essentially those described previously [2, 3, 4]. Approximately 0.2-g. samples of wool were immersed in sulfuric acid containing surface active agent at concentrations (of active ingredient) of 0.0, 0.001, 0.003, 0.01, and 0.03% (wt./vol.) for 15 min. The use of solutions of equal concentrations by weight rather than by molarity was dictated by the lack of quantitative information regarding many of the compounds tested. Excess acid was removed by centrifuging and, as liquor retention is affected by the concentration of surface active agent, different concentrations of acid in the range 14.5–20.6% (wt./vol.) were used to give a final acid content of about 12.5% on the neutral oven-dry weight of all samples. The wool was heated for 45 min. in air at 105° C. using a ventilated laboratory oven provided with a fan; it was neutralized, dried, and conditioned overnight at 20° C. and 70% RH.

Fiber strength was assessed manually by pulling the samples between finger and thumb. The unlabeled samples were presented to the assessor in random order and interspersed with untreated samples to check the validity of the assessment. Additional samples were treated with the acid solutions, centrifuged with the test samples, and assayed for residual H_2SO_4 by the method of Barritt [1].

Results

The results with different types of surface active agent are summarized in Table I. The fatty acid monoesters of polyoxyethylene, higher alkyl ethers of polyoxyethylene, and aryl alkyl ethers of polyoxyethylene gave similar results. There was a steady increase in strength rating with increasing concentration of the agent to values approaching the mean assessment for untreated wool at a concentration of 0.03%. As would be expected, the scatter of results was greatest at the lower concentrations in each case, hence the greater variance of strength ratings for lower concentrations of the surface active agents.

Nonionic agents in which polyoxypropylene constitutes the lipophilic part were obviously ineffective in protecting wool even at the higher concentrations. Of the 16 compounds of this type, only 2 showed some protective effect at concentrations of 0.03%. Although many anionic agents provided protection at a concentration of 0.03%, they afforded little protection at low concentrations. Cationic agents, on the other hand, were much more effective and compared favorably with the better types of nonionic agents. At the higher concentrations used, many surface active agents decreased damage to the level where it was no longer apparent using a tactile test.

The nonionic agents giving observable protective effects have been subdivided according to the nature of the lipophilic portion. The means of two strength ratings of wool samples carbonized in acid solution containing the various agents belonging to each class of compound are related to the mean number of oxyethylene units in each compound in Figures 1–5. With polyoxyethylene nonylphenyl compounds (Figure 1) the strength rating increases as the oxyethyl-

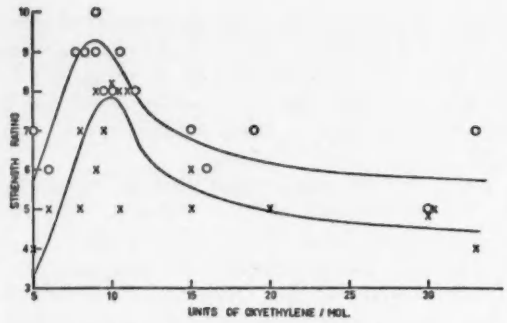

Fig. 1. The relationship between the strength of wool samples carbonized with sulfuric acid containing nonyphenyl polyoxyethylene compounds and the number of oxyethylene units in the molecule (five manufacturers). ×, 0.001%; ○, 0.003%.

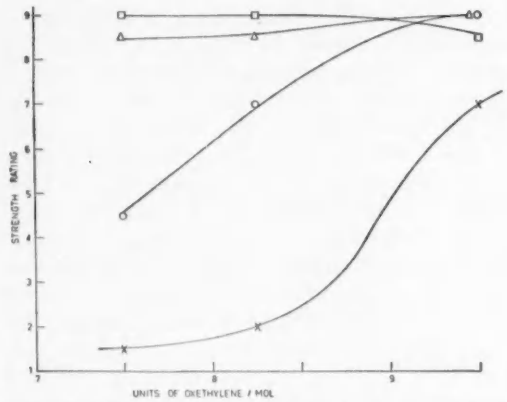

Fig. 2. The relationship between the strength of wool samples carbonized with sulfuric acid containing octylphenyl polyoxyethylene compounds and the number of oxyethylene units in the molecule (two manufacturers). ×, 0.001%; ○, 0.003%; △, 0.01%; □, 0.03%.

ene units in the molecule increase from 5 to about 10 and then decreases slowly with further increase in the number of oxyethylene units. Polyoxyethylene octylphenyl compounds (Figure 2), polyoxyethylene octylcresyl compounds (Figure 3), and polyoxyethylene esters of stearic acid (Figure 4) show a similar increase in effectiveness as the mean number of oxyethylene units increases from 7.5 to 10, from 2 to 15, and from 6 to 14 respectively. Unfortunately, compounds with longer polyoxyethylene chains were not available in these classes of compound. With the mixed oleyl-cetyl or cetyl ethers of polyoxyethylene, the results were less clearcut but, in general, the strength rating appeared to increase with increasing length of the polyoxyethylene chain.

Strength ratings obtained with related compounds belonging to a series produced by a single manufacturer usually fell on a fairly smooth curve. In other instances, compounds which were stated by two manufacturers to have the same lipophilic moiety and the same mean number of oxyethylene units gave results which were significantly different, particularly at the lower concentrations tested. An example of this occurs with nonylphenyl compounds having a mean of 10.5 oxyethylene units with concentrations of 0.001% (Figure 1). Repetition of such experiments showed that the differences in results were due to differences in composition of the agents and not to variation in estimates of strength. The presence of impurities, or differences in the spread of molecular weights about the mean, may be responsible for these differences.

Discussion

It is apparent from Table I that those commercial surface active agents which have polyoxypropylene as the lipophilic group give no apparent protection to the wool against the action of sulfuric acid in carbonizing in the range of concentrations tested. Surface active agents containing a hydrocarbon lipophilic portion are all effective protecting agents if the number of oxyethylene units in the hydrophilic portion is near the optimum.

No direct evidence concerning the mechanism of the protective action of surface active agents in car-

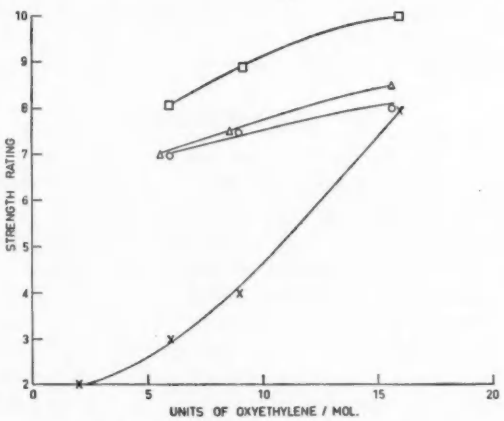

Fig. 3. The relationship between the strength of wool samples carbonized with sulfuric acid containing octylcresyl polyoxyethylene compounds and the number of oxyethylene units in the molecule (one manufacturer). ×, 0.001%; ○, 0.003%; △, 0.01%; □, 0.03%.

bonizing has yet been obtained, but certain conclusions appear to be possible by a consideration of two possibilities.

1. Surface active agents may facilitate spreading of the acid over the surface of the fibers, thereby eliminating local concentrations of sulfuric acid which would cause weak spots in the fibers.

2. The surface active agents may be adsorbed in such a manner as to prevent access of the acid to reactive sites within the fiber. The latter effect may be brought about by adsorption at the surface or by adsorption at specific sites within the protein structure. The possibility of the latter effect initiated the original tests with surface active agents [2].

The results of the present investigation suggest that surface active agents do not bring about their effect by distributing the acid over the surface of the wool. The polyoxyethylene-polyoxypropylene compounds at the experimental concentrations are reputed to reduce the surface tension of water at 25° C. to values in the range 39–62 dynes/cm. and at higher temperatures much lower values are recorded, yet these provide no significant protection. Other types of agent at concentrations which reduce the surface tension to similar levels give strength ratings of 5, 6, or 7 (Figure 6). Hence, although this figure indicates that a relationship exists between the strength rating and the ability of hydrocarbon ethers of polyoxyethylene to reduce the surface tension, this relationship does not apply to the condensates of polyoxyethylene and polyoxypropylene. Furthermore, the surface tension of sulfuric acid decreases markedly with increasing concentration, so that even in the absence of surface active agent there will be a tendency for the acid to spread evenly over the surface of the fibers as it becomes more concentrated.

Apart from the obvious chemical differences between the suitable and unsuitable types of agent, there is also the difference in mean molecular weight. The polyoxyethylene-polyoxypropylene compounds were all of high molecular weight (1,500–27,000). As the concentrations in Table I are on a percentage

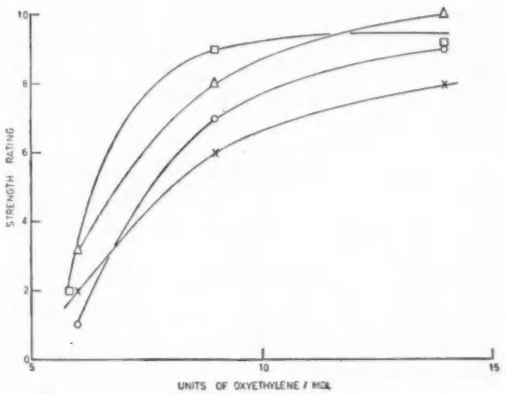

Fig. 4. The relationship between the strength of wool samples carbonized with sulfuric acid containing polyoxyethylene esters of stearic acid and the number of oxyethylene units in the molecule (three manufacturers). ×, 0.001%; ○, 0.003%; △, 0.01%; □, 0.03%.

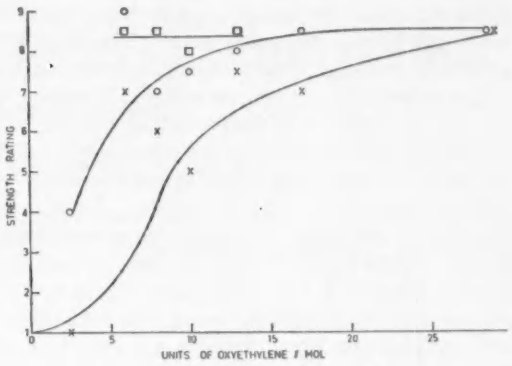

Fig. 5. The relationship between the strength of wool samples carbonized with sulfuric acid containing oleyl-cetyl polyoxyethylene compounds and the number of oxyethylene units in the molecule (three manufacturers). ×, 0.001%; ○, 0.003%; □, 0.03%.

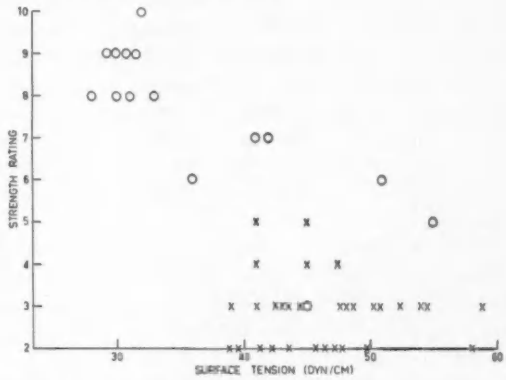

Fig. 6. The relationship between surface tension of 0.001% solutions of surface active agents at 25° C. and strength ratings for wool samples carbonized in sulfuric acid containing 0.001% of surface active agent. Surface tension data were supplied by the manufacturers. ×, condensates of polyoxypropylene and polyoxyethylene; ○, hydrocarbon ethers of polyoxyethylene.

basis, the molar concentrations of the higher molecular weight compounds would be low. However, this difference in molar concentration cannot explain the major differences in strength rating. Reference to Figures 1–5 will show that most of the effective agents had molecular weights in the range 500–1,200, yet many of these compounds at concentrations of 0.001% were more effective than any of the polyoxyethylene-polyoxypropylene compounds at concentrations of 0.03%. If, on the other hand, it is necessary for the surface active agent to enter the fiber to provide effective protection, the ineffectiveness of the polyoxyethylene-polyoxypropylene compounds may be explained on the basis of molecular size.

Variations in molecular weight of compounds in any one class must be borne in mind when interpreting Figures 1–5. There is in fact a small decrease in molar concentration with increasing numbers of oxyethylene units. Therefore the increase in strength rating with increasing length of the polyoxyethylene chain on a molar basis would be slightly greater than that shown in the figures. The decrease in strength as the number of oxyethylene units increases above 10 in Figure 1 would be slightly less. However, a comparison with the curves for other concentrations shows that variation in molar concentration does not account for this decrease.

Table I shows that cationic agents are far more effective than anionic agents on a percentage basis, and this also applies when solutions of equal molarity are considered. It seems probable that the anionic agents are strongly adsorbed at the ionized side chains of the wool and are no longer available for adsorption at the sites which affect the damaging attack of the acid on the wool. Cationic agents in acid solution and nonionic agents, which are not appreciably reduced in concentration by adsorption on the wool, would not be affected in this manner. For this reason also, anionic agents do not provide satisfactory protection under industrial conditions because the acid bowl is rapidly depleted of surface active agent as the wool is passed through the acid. If then the protective action of wetting agents takes place within the fiber, it follows that the sites of this effect are not the ionic centers at which anionic agents are adsorbed.

There are also observable differences in the color of the wool after carbonizing in the presence of different agents. It has not been possible to relate this effect to the chemical structure of the various types of agent used, and it may in fact be largely determined by the purity of the agent used. It would be advisable for prospective users of surface active agents in carbonizing to conduct laboratory tests such as those described above using a range of otherwise suitable agents to determine their relative merits as regards color of the carbonized wool. This would also serve as a useful check for protection against damage.

It should be emphasized that the concentrations of surface active agents needed to provide protection against damage will depend on the grease content of the wool entering the acid bowl. At concentrations such as 0.001 or 0.003%, protection can be expected only with grease-free wool.

Acknowledgment

The authors' thanks are due to the manufacturers and distributors of surface active agents who provided samples and details of their products. Assistance was received from Antara Chemicals (through Union Carbide Aust. Ltd.), Atlas Powder Co. (through C.S.R. Chemicals Pty. Ltd.), John Beith & Co. Pty. Ltd., Colin Campbell Pty. Ltd., Chemical Materials Ltd., Ciba Pty. Ltd., David Chemicals Pty. Ltd., Gardinol Chemical Co. (A'sia) Pty. Ltd., Geigy (A'sia) Pty. Ltd., Imperial Chemical Industries Ltd., J. Kitchen and Sons Pty. Ltd., Magnus Chemical Co. Pty. Ltd., Edgar I. Noble and Co., Polymer Corporation Pty. Ltd., Shell Chemicals (Aust.) Pty. Ltd., Union Carbide Ltd., Victoria Chemical Co. Pty. Ltd., and Henry H. York and Co. Pty. Ltd.

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Heat Induced Chemical Changes in Cotton Fiber

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SINCE the introduction of artificial drying in ginning, cotton mills have complained about overdried cotton and its effect on cotton spinning. Studies on gin-dried cotton indicate there are more ends down and in some cases weaker yarn [2, 3]. Some preliminary work by the authors on overdried cotton also indicated structural changes in the fiber as measured by decreased moisture regain.

Since it is difficult to know the history of cotton fiber and conditions under which it was ginned, laboratory studies were made on cotton of known history, physical condition, and characteristics to determine how heat drying damages cotton fiber during ginning and mill processing.

Materials and Methods

The cottons used in the laboratory tests were experimental upland cottons from the Texas Agricultural Experiment Station at Lubbock, Texas. An effort was made to obtain cottons with a minimum of field weathering. Micronaire readings on the fibers ranged from 2.6 to 5.4, representing cottons of three stages of maturity with a good range for test drying (Table I). An early and a late harvested cotton from a producer in the Lubbock area was ginned with no heat, at 175° F., and at 350° F. (80° C. and 175° C.) respectively. Tests were made on these samples along with the laboratory heated cotton to obtain additional information on overdrying.

Prior to heat treatment in the laboratory, the cottons were allowed to come to a moisture equilibrium of about 4%. Heating in the laboratory was conducted in a forced draft oven at 70°, 80°, 90°, 110°, 150°, and 200° C. The duration of heating was 10, 20, and 30 min. An unheated sample of the three different degrees of development was used for comparison. After heating, samples again reached a moisture level of about 4% before chemical tests were made.

Tests used to determine changes in cotton due to drying were as follows.

1. Moisture regain
2. Dye adsorption
3. Degree of nitration
4. Degree of polymerization
5. Degree of swelling
6. Carbonyl groups
7. Carboxyl groups

Methods for dye adsorption, degree of nitration, degree of polymerization, and carbonyl and carboxyl groups were described in a previous paper by Hessler [1]. Moisture regain was determined on a 1.0-g. sample which was allowed to reach saturation at 65% relative humidity and 70° F. After weight at moisture equilibrium was obtained, the samples were dried at 110° C. and reweighed. For the moisture regain rate study, the cotton was desiccated to dryness at room temperature. Degree of swelling is based on the method of Richter at al. [4]. A 0.5-g. sample of raw cotton was soaked in water for 1 hr. The water was removed with isopropyl alcohol and isopropyl ether to the point of dryness and the sample was then allowed to take up isopropyl ether to

TABLE I. Fiber Properties of Laboratory Heated and Gin Heated Cotton

Cotton classification	Length, in.	Strength, psi × 1000	Micronaire fineness	Amorphous cellulose, %	Cellulose, %
Fine	0.92	72.3	2.6	19.2	89.9
Medium	0.98	74.6	3.8	12.0	92.3
Coarse	1.02	77.0	5.4	9.3	94.0
Early*	1.04	79.9	4.0	11.6	92.1
Late*	0.98	70.2	3.1	16.0	90.7

* Refers to harvest of gin heated samples.

the saturation point. Surface ether was removed by pressing the sample between paper towels and holding the sample in front of an air current until the odor of ether disappears. Samples were placed in a desiccator to come to equilibrium, weighed, and oven-dried to remove ether from the fiber. The difference in weight between the ether saturated fiber and the fiber from which the ether has been removed is a measure of the degree of swelling.

Results

Several tests were made on cotton which had been heated up to 30 min. at temperatures ranging from 70° to 200° C. The purpose of the tests was to determine structural changes in cotton fiber and translate these changes to gin drying at comparable temperatures. Moisture regain is very sensitive to previous heating of the cotton and the degree of fiber development (Figure 1). The time of heating had little effect until temperatures were in the vicinity of 90° C. (Figure 2). A 20-min. heat duration was used for the remainder of the tests. Tests on an early (Mic. 4.0) and a late ginned cotton (Mic. 3.1) did not indicate differences as great as might be expected from the results obtained from laboratory heated cotton (Figure 3). Apparently, the time element is important in gin drying. The rate of moisture regain on cotton samples heated for 20 min. over a range of temperatures up to 200° C. shows a marked falling off for the 110° C. and 200° C. samples (Figure 4). There is about 0.50% difference in moisture regain between the unheated sample and the sample heated to 200° C. up to the first 2 hr. After that period of time, the spread becomes greater until 0.85% difference is reached within 3 hr.

The swelling of cotton is a function of structure. The fine cotton with an amorphous cellulose content of 19.2% shows a degree of swelling from over 12.3 ml./100 g. with no heat to around 11.7 ml./100 g. when heated from 150° to 200° C. for 20 min. (Figure 5). The coarse cotton had an amorphous cellulose content of 9.3%; the medium cotton, 12.0%. The medium cotton dropped in degree of swelling from slightly less than 10 ml./100 g. to 8.6 ml./100 g. after heating to a high temperature. The coarse cotton which had a degree of swelling of 9.6 ml./100 g. with no heat dropped only slightly on heating to 200° C. That ginned samples are sensitive to this test is shown in Figure 6. The early cotton showed a decrease of over 2 ml./100 g. in degree of swelling on heating to 80° C. in the gin. The higher heat had no effect on degree of swelling. The late cotton showed a continued drop in degree of swelling with heat applied at the gin.

Dye adsorption decreases with heating (Figure 7). The greatest decrease came from 110° to 200° C.

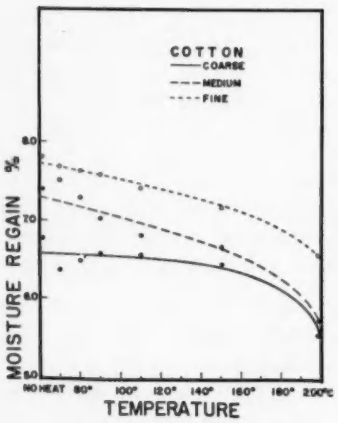

Fig. 1. Moisture regain changes in cotton heated for 20 min. at different temperatures.

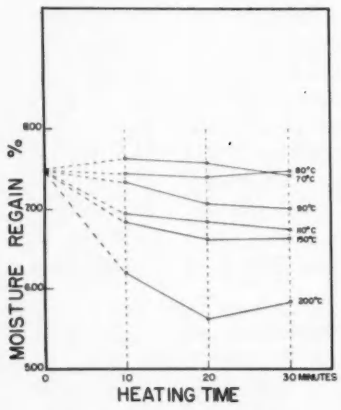

Fig. 2. Effect of variation of the heating interval on moisture regain of medium fineness cotton.

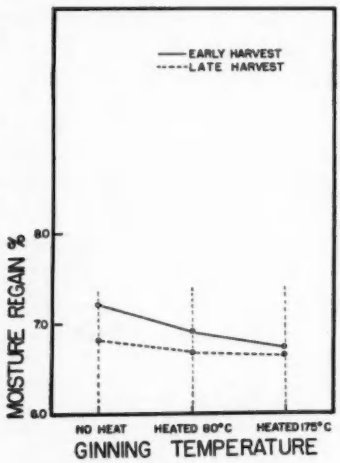

Fig. 3. Changes in moisture regain of early and late harvested cotton by gin drying at conventional (80° C.) and high heat (175° C.).

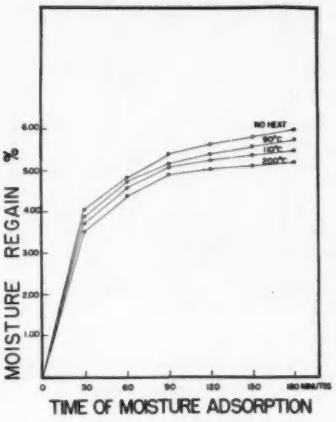

Fig. 4. The rate of moisture regain of medium fineness cotton as influenced by temperature of heating.

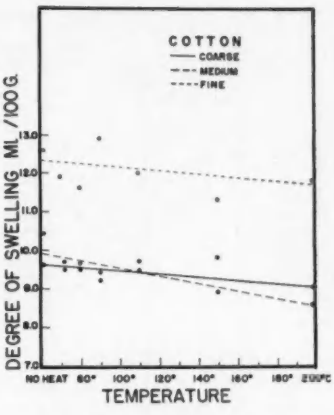

Fig. 5. The effect of temperature of heating on the degree of swelling for three different cottons.

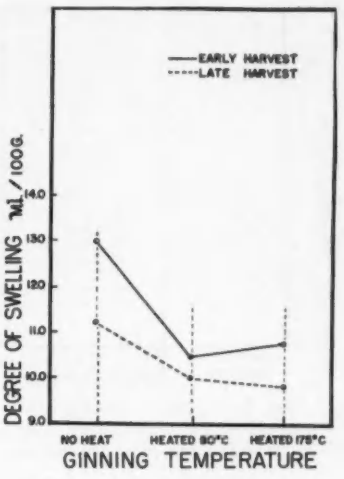

Fig. 6. Effect of ginning temperature on the degree of swelling of early and late harvested cotton.

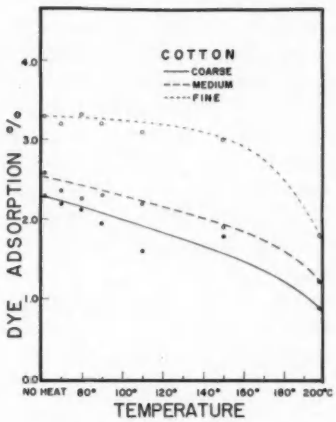

Fig. 7. Changes in dye adsorption by heating cotton of different fineness for 20 min.

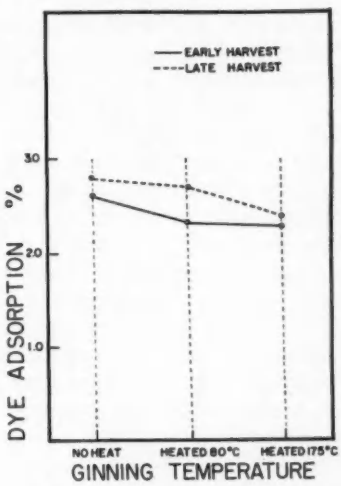

Fig. 8. Effect of ginning temperature on the dye adsorption of early and late harvested cotton.

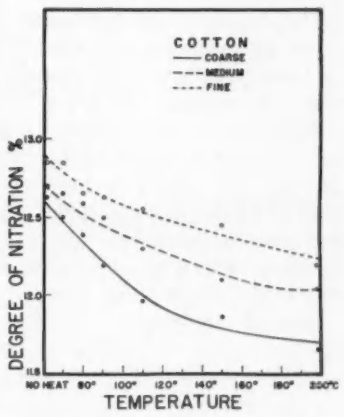

Fig. 9. The influence of 20 min. heating on the degree of nitration of cottons of different fineness.

As in the case of moisture regain, the cottons having loose structure took up the most dye, which also was true for the gin heated samples (Figure 8). Heating cotton in the gin has definitely affected dye adsorption.

Observations over a period of years by the authors indicate that nitration of cotton is less after heating. The fine cotton had the highest degree of nitration, followed by medium and then coarse cotton (Figure 9). Heat decreased the degree of nitration more in the coarse cotton than in the other two samples in the test. The effect of nitration on gin dried cotton is not great at the conventional drying temperature of 80° C. but decreases noticeably at 175° C. (Figure 10).

Heat changes the polar groups in cotton, and the extent of this change is a function of temperature (Figure 11). Carboxyl groups in the gin-heated

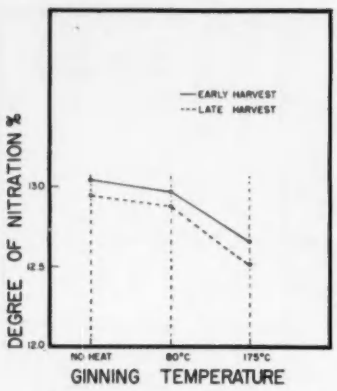

Fig. 10. Effect of ginning temperature on the degree of nitration of early and late harvested cotton.

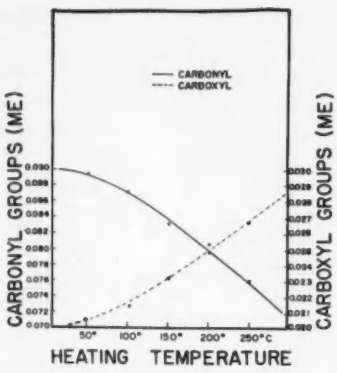

Fig. 11. Changes in polar groups of cotton fiber by heating at increasing temperatures for 20 min.

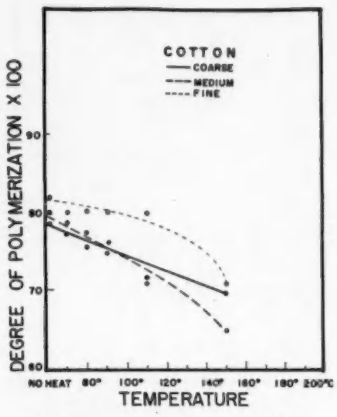

Fig. 12. The change in degree of polymerization of cotton by heating at different temperatures for 20 min.

samples increased slightly, whereas carbonyl groups remained about the same.

The degree of polymerization is not greatly affected for the fine cotton until 110° C. is reached; then the DP shows a progressive decrease (Figure 12). The medium and coarse cotton shows a progressive decrease in DP from the lowest to the highest temperature. Samples heated to 200° C. were only partially soluble in butyl acetate, which indicates additional changes in the cellulose molecule at the higher temperatures. On the ginned dried samples both early and late cottons show a substantial drop in DP for the highest heat (Figure 13).

Strength measurements decrease with increased heat up to 150° C. and then a substantial decrease at 200° C. for both 0 gauge and $\frac{1}{8}$-in. gauge (Figure 14). Strength measurements were made on the medium cotton only. No significant differences in Pressley strength were found for the samples heated at the gin when compared to the unheated sample at either gauge length.

Discussion

The fine, medium, and coarse cottons were chosen for these tests to give a range of physical structure. The fine cotton has a thin-walled, loose structure, as is shown by the high amorphous cellulose content of 19.2% (Table I). The coarse cotton has a thick-walled, highly crystalline structure with an amorphous cellulose content of 9.3%. The medium cotton will fall in between structurally, as is shown by its amorphous cellulose content of 12.0%. These cottons will cover the range of cottons found in mill operations fairly well. The results from adsorption and swelling data indicate that the severity of heat damage will be a function of fiber development. The highly amorphous cottons will be affected most in the loose-structure regions, where adsorption takes place. The fine and medium cottons were affected about the same in their ability to adsorb moisture and to swell after heating, whereas the coarse, highly crystalline cotton showed little effect of temperature on swelling. The coarse cotton lost much of its ability to regain moisture at 200° C. In the finer, more loosely structured cottons, the ability to take up moisture and swell the fiber will affect physical properties such as flexing, elongation, etc. to a greater extent than in the coarser cotton. Since heat decreases these properties, the difficulties encountered in spinning may be explained by considering the changes in physical properties due to the loss in the ability of these fibers to regain moisture. The amount of swelling on the various fibers also confirms these findings. The more a fiber is able to swell, the greater would be its ability to flex and absorb the shock of give and take in processing cotton for yarn. In addition to the amount of moisture adsorbed, the rate at which adsorption takes place may be important in conditioning cotton in the mill. Tests indicate that an overheated cotton will regain moisture at a slower rate; therefore the amount of moisture taken up could become critical in overheated cotton (Figure 4).

The ability of a cotton to take up dye is also a

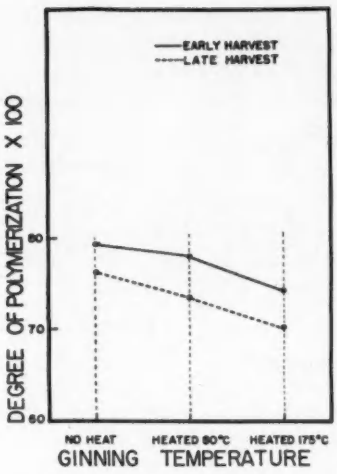

Fig. 13. Effect of ginning temperature on the degree of polymerization of early and late harvested cotton.

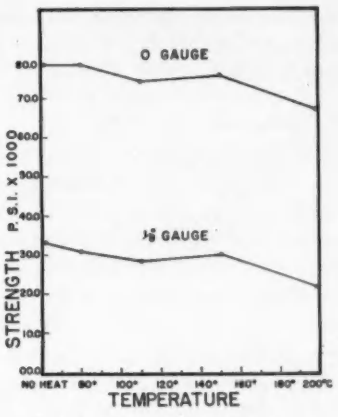

Fig. 14. Loss in strength of medium fineness cotton heated at different temperatures.

function of structure (Figure 7). The data indicate that dye adsorption is slightly affected at temperatures below conventional gin drying temperatures of 80° C.; however, cotton heated above 90° C. shows a marked decrease in dye adsorption. Although the dye molecule is larger than the water molecule, the effect of heat on the amorphous region of the fiber appears to be the same.

Nitration of a fiber is a chemical reaction. The degree of nitration is a function of wall thickness, structure, and the amount of extraneous material other than cellulose in the fiber. Heat has affected the degree of nitration to about the same extent for all fibers (Figure 10). Any decrease in nitration of the coarser fiber may be explained by taking into account the fewer and smaller amorphous regions which may be decreased more by heat in proportion to the looser-textured cottons. Nitration is facilitated by swelling in the nitration reagent. If heat, as appears likely, has affected the ability of the fiber to swell, the effect on lower nitration of heated fibers may be explained.

The change in polar groups in cotton from heating is apparently an oxidation, since carbonyl groups decrease and carboxyl groups increase. Thus, heating of cotton may be expected to affect the reactivity of the fiber to adsorption and chemical reaction.

High heat has decreased the degree of polymerization which could weaken the fiber and possibly explain some of the effects of overdrying at the gin on mill spinning (Figure 11). The Pressley strength results at both 0 and $\frac{1}{8}$-in. gauge show loss of strength. The loss in ability of the heated fiber to swell and take up moisture may account for these strength differences (Figure 13).

There were noticeably more erratic results in the finer cotton to certain test measurements. A possible explanation is the lack of uniformity in the more underdeveloped cottons. Furthermore, the amount of noncellulosic to cellulosic materials is greater in the fine cottons. The coarse cotton had 94% cellulose, whereas the fine cotton had only 89% cellulose.

Some of the inconsistencies between the early and late harvested samples may be accounted for by differences in field weathering. The early cotton had a minimum of weathering, whereas the late cotton was subject to considerable weathering and rain. Since the late cotton will be less developed and show lower cellulose content, a loss of extraneous material other than cellulose may be expected. Thus, the reaction to adsorption may be altered by field weathering [1].

Even though, in gin drying, cotton is in contact with the heat for only a short time, most of these dryers are very efficient and effective in heating and drying cotton. In the tower dryer as used on the gin-heated samples in this experiment, the cotton is in a state of violent motion due to the baffling in the

dryer. Under these conditions, the cotton is in contact with hot surfaces which are better conducters and heat faster than hot air.

Summary

Cottons of various degrees of development were subjected to different amounts of heat in the laboratory. The data indicate that physical and chemical changes will to some extent depend on the physical nature of the fiber. Evidence from adsorption and swelling data suggest structural changes in the fiber which alter the ability of the fiber to take up moisture and to swell. Chemical reaction as measured by the degree of nitration also indicates structural changes due to excessive heat. Degree of polymerization decreases at the higher temperatures in oven heating and gin drying. A slight decrease in tensile strength was noted in drying at moderate temperatures, whereas a substantial drop occurred in drying at the higher temperatures.

In some cases the laboratory results may be translated to gin drying results and offer a possible explanation of why excessive heat in ginning may reduce the efficiency in mill processing in spinning for yarn.

Acknowledgment

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Infrared Study of Oxidized Keratin

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Abstract

The infrared spectra of oxidized human hair, callus, and wool were examined. An absorption band at 9.6 μ was observed in the spectra of all the oxidized species, whereas the untreated keratin did not absorb at that wavelength. The nature of the group responsible for the band is not clear, but it was established that infrared absorption by keratin at 9.6 μ is a specific test for a prior oxidative treatment.

Introduction

Previous studies have shown that the cystine group in keratin is susceptible to attack by oxidizing agents; when the oxidized keratin is hydrolyzed, cystine disulfoxide [6, 8], cysteic acid [2, 6], and sulfate ion [6] are among the reaction products. The nature of the sulfur–oxygen intermediate formed in the keratin during the oxidation has not been elucidated, and it was thought that an infrared study might provide an answer.

Since cysteic acid can be isolated from a hydrolyzed portion of bleached wool, it has been assumed that oxidizing agents such as alkaline hydrogen peroxide can split the disulfide bond in keratin and oxidize the sulfur portion of the molecule to a sulfonate group. An alternate mechanism, which would result in the isolation of the same product, would involve the addition of one or more oxygen atoms to the disulfide group so that perhaps sulfoxide or sulfone linkages are formed. Upon hydrolysis of the protein, the intermediate could be converted to cysteic acid. Since sulfonate, sulfoxide, and sulfone groups can be distinguished from one another by their infrared absorption [4], it was anticipated that the infra-

red spectrum of a particular oxidized keratin sample would yield information about the state of the sulfur atoms.

Experimental

Human hair was chosen as the keratin substrate in almost all of the experiments; in addition, the infrared spectra of oxidized callus and wool were examined. Infrared spectra were obtained with the samples pressed into potassium bromide pellets. To prepare the hair and wool for the scan, the sample was ground with a mortar and pestle under a mixture of acetone and dry ice; in this way, possible chemical changes arising from the high temperatures encountered in other typical grinding apparatus, such as a ball mill, were minimized.

Since preliminary experiments disclosed that the spectrum of bleached hair was different from that of an untreated sample, the changes in spectra as a function of magnitude of oxidative treatment with alkaline hydrogen peroxide were studied. In addition, the changes brought about by hypochlorite, permanganate, peracetic acid, and acidic hydrogen peroxide were examined.

Human hair was obtained from DeMeo Brothers, New York. Different samples were oxidized with the following reagents:

1. Three different solutions of hydrogen peroxide, each 3.5 *N*, one adjusted to pH 11.5 with sodium hydroxide, another to pH 9.5 with ammonia, and one to pH 4.5 with hydrochloric acid and sodium acetate. Samples were immersed for 1 hr. and then allowed to air dry for about 2 hr. The hair was then rinsed well with distilled water and dried.
2. Hydrogen peroxide, 3.5 *N*, adjusted to pH 9.5 with ammonia. Two series of samples were prepared; in the first, the samples were immersed for 10 min. and then allowed to air dry. In the second series, the 10-min. immersion was repeated after the initial reaction and air drying. These samples were again allowed to air dry and then rinsed well with distilled water and dried. Nine different lots of hair were treated in this manner.
3. Sodium hypochlorite, 3 *N*, pH 12. Samples were also oxidized with solutions adjusted to pH 9.5 with hydrochloric acid, pH 7 with hydrochloric acid plus sodium bicarbonate, and pH 4 with hydrochloric acid and sodium acetate. Samples were immersed for 10 min. and then allowed to air dry. The hair was then washed well with distilled water and dried.
4. Potassium permanganate, 1.0 *N*, in 0.1 *N* hydrochloric acid. The sample was immersed in the solution for 30 min., then rinsed well with distilled water and allowed to dry.
5. Peracetic acid, 3.5 *N*. The sample was immersed in the solution for 1 hr., allowed to air dry, and then rinsed with distilled water.

Human callus, prewashed with petroleum ether and acetone, was treated for 1 hr. with 3.5 *N* hydrogen peroxide adjusted to pH 9.5 with ammonia.

Fine Australian wool, prewashed with diethyl ether, ethyl alcohol, and water, was treated for 1 hr. with 3.5 *N* hydrogen peroxide adjusted to pH 9.5 with ammonia.

All of the treated samples were prepared for infrared analysis in the following manner. Approximately 0.1 g. of material was cut into 0.5-cm. lengths and placed into a mortar containing 25 ml. of acetone and excess dry ice mixture. The sample was ground with a pestle for 1 min., after which time several grams of dry ice were added to the mortar. This procedure was repeated twice, so that the total grinding time was 3 min. The coarse particles were then allowed to settle to the bottom of the solution and the supernatant liquid transferred to an evaporating dish by means of a medicine dropper; the gross material remaining in the mortar was discarded. The acetone in the evaporating dish was allowed to evaporate in a hood; the resulting residue was dried for 1 hr. under vacuum at room temperature. Approximately 5–10 mg. of material amenable to infrared analysis by the potassium bromide technique was isolated.

Potassium bromide pellets of the samples were prepared by mixing 1 mg. of material with 400 mg. potassium bromide for 10 min. in a Perkin-Elmer vial vibrator and then subjecting the mixture to 23,000 lb. of pressure in a Perkin-Elmer evacuable die. The spectra were obtained with a Perkin-Elmer Model 21 Spectrometer equipped with sodium chloride prism.

Results and Discussion

The spectrum of a typical untreated hair sample is shown in Figure 1, Curve A. Structural assignments of some bands have been made [4, 5]; thus,

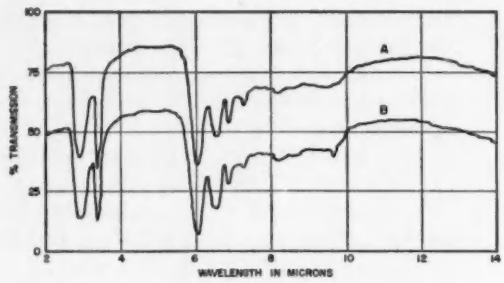

Fig. 1. The infrared spectra of hair. A, Untreated; B, hydrogen peroxide-treated.

the bands at 3, 3.4, and 6μ are due to NH, CH, and C=O stretching vibrations, respectively, while those at 6.5 and 6.9μ are associated with NH and CH_2 deformation modes [3].

To ascertain whether the presence of acetone during the grinding period was causing changes in the infrared spectrum of the keratin, several samples were ground under liquid nitrogen. The spectra obtained in these instances were identical in all respects with those samples ground under acetone. However, since it was more convenient to work with acetone–dry ice mixtures rather than liquid nitrogen, the former grinding medium was used to prepare the keratin for infrared analysis in subsequent experiments.

The spectra of wool and callus were essentially the same as that of human hair. However, the C=O stretching vibration at 6μ was less intense in the wool spectrum than in the other two, while a weak band at 8.1μ in the spectra of callus and of hair was not apparent in the spectrum of wool. These differences may be due to variations in sample preparation but, in any case, the spectra of the three keratins are very nearly identical.

Curve B in Figure 1 depicts the spectrum of hair oxidized with 3.5 *N* hydrogen peroxide at pH 9.5 for 1 hr. A comparison of Curves A and B discloses that the two spectra are essentially identical, with the exception of an absorption band at 9.6μ in the spectrum of the bleached sample. The spectra of callus and wool, treated in the same manner as the hair sample described above, differed from those of the respective untreated keratin samples in just the same way; that is, the only difference observed was in the region of 9.6μ, at which point the oxidized samples displayed weak absorption.

The effect of changes in the pH of the hydrogen peroxide solution upon the intensity of the 9.6μ absorption in oxidized hair is shown in Table I. Absorbance values were obtained by the base-line method [10]. The results are in agreement with the observation that the reaction of keratin with hydrogen peroxide is slow except in alkaline solution [1].

In Table II are shown the results obtained with nine different lots of hair, each lot containing an untreated, a bleached, and a twice-bleached sample. The pH of the hydrogen peroxide solution used for the treatment was 9.5.

The data show that, in every case, untreated samples did not absorb at 9.6μ, while bleached samples did. In addition, the intensity of absorption was related to the severity of the bleaching treatment. This fact lends support to the thesis that the absorption at 9.6μ is due to some new functional group in the keratin, produced by the action of hydrogen peroxide, and that a previous hydrogen peroxide treatment can be detected by infrared spectrometry.

In hydrogen peroxide-treated hair, the strongest absorbance at 9.6μ observed in samples which had been repeatedly bleached and air dried was approximately 0.08. Of significance was the fact that in this instance of excessive treatment, the spectrum of the bleached hair was not altered in any way from that of virgin hair other than at 9.6μ.

Hair samples treated with sodium hypochlorite displayed absorption at 9.6μ in every case except when

TABLE I. Effect of pH of Hydrogen Peroxide Solution on Intensity of Band at 9.6 μ

pH of peroxide solution	Absorbance at 9.6 μ
4.5	0.000
9.5	0.046
11.5	0.050

TABLE II. Absorbance at 9.6 μ as a Function of Hair Lot and Peroxide Treatment at pH 9.5

	Absorbance		
Lot	No treatment	Bleached once	Bleached twice
1	0.000	0.008	0.017
2	0.000	0.009	0.018
3	0.000	0.007	0.008
4	0.000	0.006	0.025
5	0.000	0.009	0.018
6	0.000	0.010	0.018
7	0.000	0.018	0.024
8	0.000	0.014	0.025
9	0.000	0.012	0.019

the pH of the treatment solution was 12. These facts are in agreement with the observation that sodium hypochlorite reacts with a lesser amount of cystine at higher pH values than at lower ones [1].

Also, hair treated with potassium permanganate exhibited absorption at 9.6μ.

The spectra of the simple compounds cystine, cystine disulfoxide, and cysteic acid were examined to determine whether clues to the nature of the group absorbing at 9.6μ would be revealed. However, as is generally the case, the spectra of the amino acids were much more complex than that of the proteins, and interpretation of the absorption bands in the 8–10μ region was not helpful in resolving the point in question.

The oxidation of cystine itself was also investigated to determine whether partially oxidized intermediates could be detected. For this purpose, an ammoniacal cystine solution was treated with a fourfold molar excess of hydrogen peroxide for periods ranging from 1 to 60 hr. and at a temperature of 25° C. The solutions were then lyophilized and infrared spectra of the recovered solids taken. In every case, the spectrum was identical with that of the starting material.

The spectrum of peracetic acid-treated hair is shown in Figure 2. It is apparent that in addition to the new absorption band at 9.6μ, there is an even stronger band at 8.5μ. This finding is in agreement with the work of Weston [9], who observed bands at both 8.5 and 9.6μ in the spectrum of peracetic acid-treated wool but no absorption at those wave lengths in virgin wool. Since it has been shown here that only one new absorption band is produced in the peroxide, hypochlorite, or permanganate treatment, it can be stated that the oxidation products formed in the keratin by the action of these reagents are not the same as those produced by peracetic acid. This conclusion is consistent with the results of Earland and Raven [7], who observed that, of the oxidizing agents used in this study, only peracetic acid was capable of producing sulfonic acid groups in the keratinlike polymer N-mercaptomethylpolyhexamethyleneadipamide disulfide.

The appearance of strong absorption bands at both 8.5 and 9.6μ in peracetic acid-treated wool and hair is indicative of the formation of either sulfonate or sulfonic acid groups [4, 9]. This assignment is consistent with the observed recovery of cysteic acid from hydrolyzed peracetic acid-treated wool samples; consequently, it is fair to assume that oxidation of the disulfide bond, with the formation of sulfonate or sulfonic acid groups, occurs during the treatment with peracetic acid. On the other hand, the absence of an 8.5μ band rules out sulfonate as a major oxidation product when wool or hair is treated with hydrogen peroxide, hypochlorite, or acidic permanganate. The nature of the intermediate is not certain, but the position of the band, 9.6μ, points to a sulfoxide group [4]. The observation of cysteic acid in the ultimate hydrolysates of hair oxidized by either peroxide, permanganate, or hypochlorite must be ascribed to further oxidation of the intermediate during or after hydrolysis.

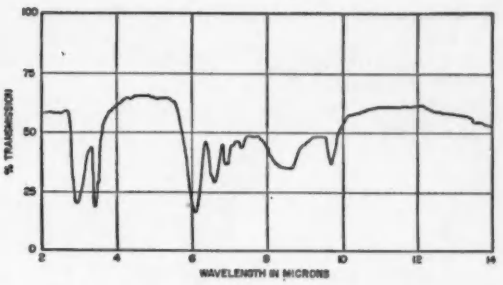

Fig. 2. The infrared spectrum of peracetic acid-treated hair.

Acknowledgment

The authors wish to thank I. M. Klotz of Northwestern University and Herman Bogaty of The Toni Company for their many valuable suggestions and comments and T. Lavine, Lankenau Research Institute, for the sample of cystine disulfoxide used in this study. This work was carried out in the laboratories of The Toni Company; the authors wish to thank The Toni Company and The Gillette Company for permission to publish.

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The paper below was first submitted for review to M. J. Coplan, whereupon it was disclosed that, unknown to the Editor, there existed an unpublished report of a study conducted by Mr. Coplan at Fabric Research Laboratories on an almost identical area. The difference in the technique applied to the problem has resulted in information in each paper that is felt to be of interest and value to readers of the Journal. Therefore, by agreement with the authors concerned, the paper by Holdaway and Laws and the report by Coplan and Golub are being carried as companion papers.

Editor

A Technique for Examining the Configuration of Fibres in Pleated Fabrics

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Abstract

A description is given of procedures and embedding media which have been used successfully to examine the "microstructure" of fabrics near pleats. The paper is illustrated with some typical photomicrographs.

Introduction

Studies of creaseproofing and permanent pleating would be greatly facilitated by experimental determination of strain levels in the individual fibers. Although theoretical estimates have been made of strain levels in deformed yarns [3], there was no report available at the time this work was undertaken of experimental studies of the mechanical deformation in bending of single fibers near a pleat. This paper describes embedding and sectioning techniques developed to examine such deformations in wool fabrics and illustrates their application to the examination of the effects of pleating and washing procedures.

Techniques

Embedding Principles and Materials

Apart from the obvious requirement of being a suitable medium for good microtomy, the embedding resin chosen should not modify significantly the fabric or fiber configuration to be studied. To meet this requirement it is desirable that (a) the resin should introduce a negligible degree of geometrical changes in the fabric structure while setting; (b) shrinkage of the resin *after it starts to thicken* should be as small as possible; (c) there should be negligible chemical reaction between the wool and the resin or its initiator; (d) polymerization should take place quickly; (e) temperature rises needed to assist polymerization or resulting from polymerization should be as small as possible; (f) the resin should form a reasonably firm bond with the surfaces of the individual fibers; (g) the resin should preferably be transparent in sections up to 30μ thick.

It has been found possible to reach a compromise which at the same time allows reasonable convenience in preparation.

The following types of resin have been investi-

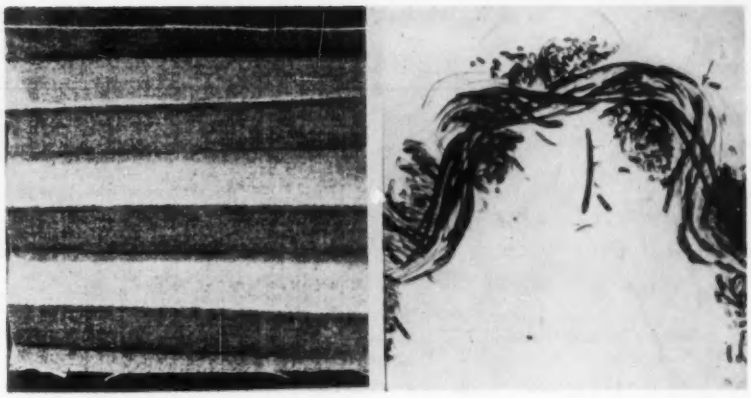

Fig. 1. Wool fabric of black and white fibers pleated by subjecting the fabric, still wet from soaking in 2% NH_3 solution, to steaming at 120° C. for 30 sec. This was released in a 1% soap solution for 5 min. at 70° C. Section ~30μ thick. Clearly visible in the photograph are warp/filling structure, twisted yarn structure, relative size of fibers in relation to yarn (closeness of packing), and bending deformations of fibers.

gated: "Araldite 103," butyl methacrylate, "Plastrene" (essentially the same as "Monsanto polyester 189," which has also been tried), polyvinyl acetate, "Bourne plastic," urea formaldehyde, and ethyl acrylate. Of these only the first three have been found reasonably satisfactory, the others mentioned being found unsuitable for various reasons. "Araldite" is a commercially available resin of the ethoxylene (epoxy) type; "Plastrene" and "Monsanto polyester 189" are commercially available resins of the polyester type.

In Table I are set out the principal properties of these three selected resin types as they relate to the objectives of the present study.

Special Procedures Employed when Embedding Creased Fabric Specimens

The primary aim must be to reduce to a minimum any distortion of the fabric structure during the mounting process or subsequently while polymerization of the embedding medium is proceeding. A small container made of pasteboard is satisfactory for holding the resin while it is setting, and may be provided with pasteboard pieces to support the fabric in position at its natural creasing angle.

Some monomers, e.g. butyl methacrylate, are initially quite free-flowing liquids and these are subject to relatively large shrinkage on polymerization. In addition, the total time for polymerization may be relatively long (of the order of 24 hr.). In such cases it is advantageous to allow the monomer to polymerize partially before using it to embed the specimen. The latter is dipped, before being embedded, in a small quantity of the monomer in order to wet it and reduce the number of trapped air bubbles. By this procedure the time during which the fabric is in contact with the chemical compound prior to setting is reduced to a minimum and volume changes in the matrix are minimized.

Control of Polymerization

Araldite (ethoxylene type resin) can be polymerized by adding accelerator and hardener compounds, in accordance with instructions issued by the suppliers. However, even with careful measurement of quantities, a certain degree of variability was detected in the final product, possibly due to variations in concentration of the inhibitor from point to point within the monomer. Where possible, in order to achieve uniformity, a reasonably large batch of resin was made up to treat as many specimens as possible at one time. Hardening progresses with time until eventually it is difficult or impossible to microtome the polymer; the optimum time is best gauged from experience, and may vary from batch to batch. After this resin had been employed for about three months, further use was discontinued, since a severe form of chemical dermatitis was experienced.

Butyl methacrylate was found to be the most suitable embedding medium. As received from the supplier, the butyl methacrylate contained 0.05% of hydroquinone as an inhibtor. It is not possible to induce polymerization in the presence of this concentration of hydroquinone, even after adding a reasonable amount of benzoyl peroxide initiator followed by the application of heat or by irradiation with ultraviolet light. Owing to the relative inconvenience of the process, removal of the hydroquinone by distilling the monomer was employed only in early

TABLE I. Principal Properties of Resins Selected for Embedding Wool Fabrics

Resin / Property	Araldite 103	Butyl methacrylate	Plastrene or Monsanto polyester 189
Coloration	Yellowish	Clear	Clear
Transparency	Imperfect	Good	Good
Stiffness (for microtomy)	Stiff to hard	Stiff (about right)	Stiff to hard or brittle (depending on time)
Shrinkage	Slight	Satisfactory, if allowed to partially polymerize before mounting fabric	Acceptable if used with butyl phthalate plasticizer
Procedure for inducing polymerization	Add 7% initiator and heat at 45–50° C.	Remove the inhibitor and add a small quantity of benzoyl peroxide and irradiate with ultraviolet light	Add 1.5% of catalyst
Typical time for polymerization, hr.	1½	20–24	2–2½
Noxious vapors	Negligible	Use in fume cupboard	Use in fume cupboard
Bonding to wool fiber surfaces	Good	Very good	Pulls away a little
Tendency to induce chemical dermatitis	Effect may be delayed but can be a serious problem. Extreme care needed to avoid touching the resin [5]	Not detected	Not detected
Ease in controlling polymerization	Fair	Good	Good

trials of this resin. An alternative procedure [1], based upon scrubbing with 10% caustic soda solution followed by distilled water and thereafter drying over anhydrous sodium sulfate, was found to remove enough inhibitor to permit satisfactory polymerization. This was induced by adding about 0.2% of benzoyl peroxide and irradiating with ultraviolet light for about 5 hr. before impregnating the specimen and 16 hr. thereafter. Since the vapor of the monomer is both toxic and unpleasant, it was found necessary to do this inside a fume cupboard.

Plastrene and Monsanto Polyester 189 resins could be polymerized without difficulty by following the instructions issued by the supplier. The process did not appear to be particularly critical, and no difficulty was experienced in reproducing results. However, the end product was usually too brittle for really good microtomy. The poor bond formed between the resin and the wool fibers allowed some of the latter to pull out of the medium when microtomed. This could be a disadvantage where something more was required than the impression left in the resin by the fiber. This resin was used to best effect to form a relatively rigid base for supporting in the microtome the smaller pieces of other softer polymers in which the pleat was embedded.

Recommended Procedure

It is recommended that specimens embedded in either Araldite or butyl methacrylate be first cut down to present to the microtome blade an approximately cylindrical block $\frac{1}{4}$–$\frac{3}{8}$ in. in diameter. The block should be supported in a casting of Plastrene. The Plastrene is cast with the face of the block standing $\frac{1}{8}$–$\frac{1}{16}$ in. clear. It was found possible to cut sections down to about 30μ in thickness in Araldite, and about 1μ with the butyl methacrylate. For the purposes of this study a thickness of about 30μ was necessary because of the near impossibility of obtaining a sectioning plane cutting through a single fiber over a satisfactory proportion of its total length in the specimen.

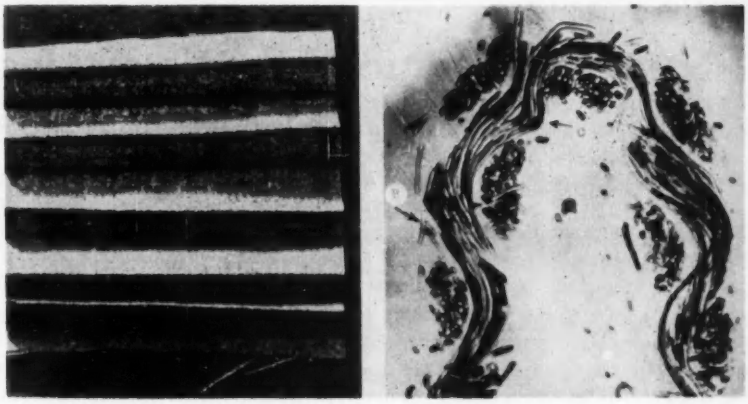

Fig. 2. Wool fabric of black and white fibers initially shrinkproofed by the "Sirofix" patented process with 3% resin addition. The pleating process was identical with that for Figure 1. Prior to examination the pleated fabric was machine washed for 30 min. in a 0.1% soap solution. In spite of the severe aftertreatment, the pleat is noticeably sharper (this being so in all sections studied). Note also the variation in local structure due to the yarn running along the line of the pleat being on the inside instead of the outside as in Figure 1.

Discussion of Typical Results

The plates used to illustrate the technique were selected to show also the improved pleat retaining properties of a fabric which has been given a prior shrinkproofing treatment. The microscope slides used for the illustrations were prepared as described above, employing Araldite as the embedding medium.

Unfortunately, photographs are incapable of illustrating all the information obtained by visual examination of specimens 20–30μ thick. In the latter case it is possible, by progressively changing focus, to follow many of the individual fibers over a satisfactory portion of their length. However, such photographs as have been made all show lengths of fiber appreciably shorter than this.

Actual bending strain levels of some typical fibers (comprising effects of weave structure, crimp, and pleating) are given in Table II. These "strains" have been estimated as the ratio of fiber radius to radius of curvature of the fiber center line. Such estimates can be regarded as approximate only ($\pm$10% accuracy). Other methods have been employed to obtain quantitative data related to pleats; an essential feature of these is the employment of statistical procedures [2, 4].

In general it is found in all such studies in which numerous sections were examined that average bending strain levels of bent fibers do not differ very markedly from those imposed by yarn bending to fit the warp/filling structure, although the difference is significant. Occasionally fibers can be found which have been deformed quite heavily in bending. These are in themselves insufficient in number to have a marked effect on the pleat retention properties of the fabric, but are usually associated with severity of the pleating process. The presence of such badly deformed fibers may indicate a degree of mechanical damage which might impair wear performance of the fabric.

TABLE II. Approximate Maximum Strain Level Values in Bending (Ratio of Radius of Fiber to Radius of Curvature) of Fibers Selected to Provide a Basis for Visual Assessment of "Strain" Levels; for This Reason Extremes Have Been Included

Fiber (see photograph)	A	B	C
Figure	1	2	2
Estimated strain level in single fibers, %	3.7	~50	~40

Acknowledgment

The fabric samples employed for Figures 1 and 2 of this paper were made available by Dr. A. Farnworth of C.S.I.R.O. Wool Textile Research Laboratories, Belmont, Geelong, Victoria, where all machine washing was also carried out.

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Manuscript received November 3, 1958.

Some Observations on Distortions at a Wrinkle

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IN THE course of a study [1] of the muss resistance of tropical worsted fabrics, these laboratories have attempted to analyze microscopically the anatomy of a wrinkle. In addition to qualitative observation of the modes of fabric, yarn, and fiber distortion, some effort has been made to quantify observed fiber bending strains. While the general program is still underway and will eventually be reported, it is felt that the early microscopical work might be of immediate interest to the readers of this Journal.

Measurement of Fiber Bending Strain

It was originally believed that, to determine fiber configurations in creased fabric, the deformed fabric specimen should be embedded and sectioned. One of the problems requiring some attention was the development of an embedding technique which would prepare the fabrics for cross-sectional study with a minimum of superimposed side effects such as fiber or yarn movement due to contraction of the embedding medium. It was considered that a desirable embedding medium would be one which sets to a proper firmness for good sectioning without evolution of heat or requiring heat for polymerization. At the same time it should have a minimal shrinkage from the liquid to solid state, evolve no bubbles, etc.

Extensive tests of various embedding media were made, particularly on the Paraplex resins (Rohm and Haas Company) and Formex C-2 (Travaco Laboratories, Inc.). However, none of these were successfully adapted because of various difficulties, and a butyl methacrylate embedding medium was employed for some of the work.

It was quickly realized that even the ideal embedment (as yet to be achieved) could not produce a sample for inspection devoid of significant obstacles to accurate determination of residual bending strains of fibers *in situ*. First, the plane projection of a fiber actually deformed in three dimensions must exhibit a distorted version of the true spatial curvature. Second, of course, any particular fiber passes out of view in the execution of its helix, rendering complete examination of even its distorted planar projection impossible. Third, in longitudinal view of a yarn of any degree of compaction, it is virtually impossible to follow the path of any but the outermost fibers.

One might minimize the effect of the first objection and eliminate the second by confining his interest to portions of fibers remaining sensibly in the plane of thin sections (i.e., about one fiber diameter in thickness or less).

By so doing, however, he is deliberately discarding large segments of those fibers which actually do remain to be measured. Moreover, the third objection cannot be readily overcome by such a method. Figure 1, showing sections from an embedded crease, illustrates some of these difficulties.

For these and other reasons we adopted another approach to the problem of determining residual fiber

Fig. 1a. Relatively thin sections of an embedded sample. Excellent view of one fiber at a pointed node, but what about the fibers that do not appear?

[1] Under sponsorship of The Wool Bureau, Inc.

curvatures. This method is not without its own flaws, but at least had the following to recommend it. Foremost, it permitted sampling *all* the fibers of a given yarn at the site of a crease. Second, it allowed for easy calculations of residual planar curvature of the deformed fibers. Third, it was rapid and convenient.

The procedure consisted of gently teasing one yarn at a time out of the previously creased or wrinkled fabric. With the yarn laid on a soft cardboard, the crease node (generally about $\frac{1}{16}$–$\frac{1}{8}$ in. of yarn) was carefully cut from the yarn with a sharp razor.

For sharply creased fabrics it was possible to verify that the projected angle of the individual yarns removed from the fabric accurately reflected the crease angle of the fabric. It is presumed, without detailed verification, that the excision of the crease node was performed without important disturbance of the curvature of the fibers in the node.

In any event, these short sections of yarn were gently dispersed with a fine needle on a drop of dry mineral oil. A cover slip was placed on the drop, thereby orienting the curved fiber fragments into planar view. It is believed that these fiber fragments continued to reflect with reasonable accuracy their *in situ* curvatures.

Fig. 1b. Part of a squared-off node; thick enough to include several fibers but too confused to measure curvatures.

Photomicrographs at 150× were made of a relatively large number of such fiber fragments removed from given yarns at the crease zone and of a similar set of fragments removed from a portion of yarn not involved in the crease. Measurement of the radius of the sharpest region of curvature in each of several fibers was made by fitting the appropriate one of a series of graduated transparent discs to the fiber photomicrograph. Focusing for photomicrographing was done upward until the outside of the Becke lines, moving inward, just coincided with the margins of the fibers. It was thus possible to measure on the photomicrographs fiber diameter at the region of highest curvature by spanning the fiber picture with finely pointed dividers placed on the outer edges of the Becke lines.

Both the smallest radius of curvature and the fiber diameter having been determined, the residual

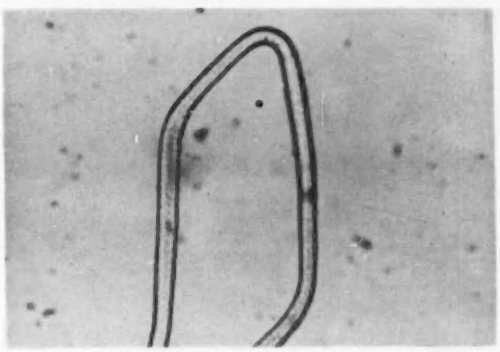

Fig. 2. Single fiber fragment excised from a pointed crease node.

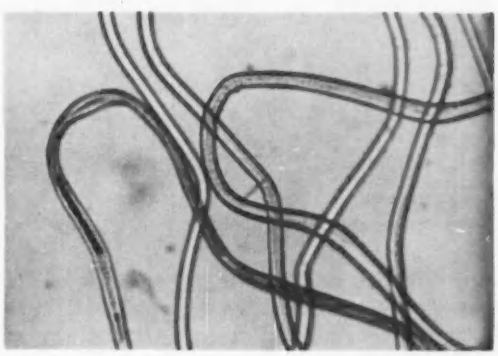

Fig. 3. Several fibers excised from a square node, illustrating curvature at *one* corner of the node as well as some of the flattened crimps of the node apex.

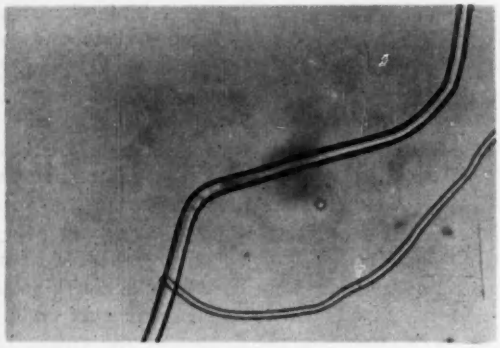

Fig. 4. Fiber excised from an uncreased region, illustrating curvature of a normal weave crimp.

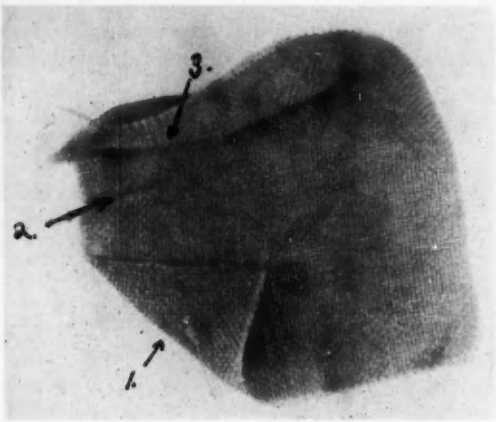

Fig. 5. Randomly wrinkled tropical worsted fabric.

average maximum bending strains in the fibers could be calculated from

$$\epsilon = \frac{d}{2\rho}$$

where ϵ = average maximum bending strain, d = fiber diameter, and ρ = radius of curvature of the bend.

The foregoing value for ϵ represents an average of the maximum tensile and compressive strains, assuming that originally plane sections remain plane after bending.

Figures 2, 3, and 4 typify the photomicrographs from which such calculations were made. The particular fabric from which these fibers had been excised was a 50 oz./sq. yd. tropical worsted that had been creased with a hot iron over a damp cloth.

Table I presents the calculated average maximum fiber bending strains from three successive yarns at the crease zone, and a fourth line gives the same information for fiber from a normal uncreased yarn crimp. It will be noted that the fiber strains in the alternate yarns 1 and 3 were found alike, while the intermediate yarn 2 was considerably higher. The reasons for this alternation will be developed shortly.

TABLE I. Average Maximum Residual Fiber Bending Strains

Yarn	Number of fibers	Average strain
Creased—1	19	0.14
Creased—2	27	0.22
Creased—3	32	0.14
Uncreased	57	0.09

An analysis of the data also indicated that on the average the coarser fibers tended to retain curvatures with larger radii. The data for yarns 1 and 3 were combined, and it was found that the 25 fibers of smallest diameter had a radius of curvature about 20% smaller than the 26 largest fibers; the difference had a high statistical reliability.

On the other hand, the average residual strain in the finer fibers was about 0.12, while that in the coarser fibers was 0.16. Thus, although their ultimate curvatures might be less, the strains imposed on and retained by the coarser fibers was greater.

Another feature observed was the decided evidence of buckling on the inner surface of the more sharply bent fibers (see Figure 3, for example). This is not too surprising when it is realized that the apparent average strain levels were upwards of 15–20%. It should be remembered that these illustrations are from sharp creases deliberately formed under heat, moisture, and pressure.

Effect of Wrinkling and Creasing on Yarn Configuration

Figure 5 shows a randomly wrinkled sample of the same fabric described above, with three creases numbered. This sample was wrinkled by stuffing it into a beaker, keeping it under a 5-lb. weight overnight at 100% RH, then drying it at 100° C. for 2 hr. Crease 1 is moderately sharp. Crease 2 contains two sharp reversals forming a "Z" in sectional view. Crease 3 is a single sharp crease. The following pertinent facts were determined.

1. The deformed configuration of yarns which cross a crease varies drastically at the crease area,

depending on whether the intersecting yarn falls on the concave or convex side of the fold. Figure 6 shows two successive warp yarns taken from Crease 3 of Figure 5. In yarn A, because of the presence of a filling yarn inside the crease, the warp yarn curves sharply, accentuating the original curvature of the particular weave crimp involved. The resulting yarn radius of curvature appears to depend upon the thickness of the filling yarn flattened by creasing. In the lower picture (yarn B, which is actually the next adjacent warp yarn), the filling yarn fell on the convex side of the crease. Here the original warp crimp was bent so that its curvature tended to be reduced and the yarn seems to have assumed a squarish shape with "corners." Figure 7 shows a sequence of warp yarns taken from the Z-type Crease 2. Close examination of the double crease shows similar alternating of adjacent yarns with high curvature and squared-off configurations in succession for each of the creases.

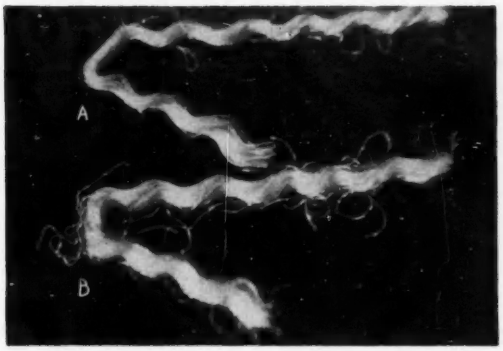

Fig. 6. Two successive yarns removed from Crease 3, Figure 5. A—Top yarn illustrates pointed node. B—Bottom yarn illustrates squared-off node.

Fig. 7. Successive yarns removed from Z-shaped double Crease 2 of Figure 5.

2. Examination of a number of such yarn successions indicates that creasing or wrinkling reduces yarn crimp one or two cycles away from the apex of the crease, as may be detected in Figure 6. Whether cross-over rigidity, the direction of pressure in creasing, or other factors prevent crimp loss from more remote crimps has not been determined.

3. Figure 8 shows a yarn from a "Z" shaped crease, 2 of Figure 5. The following is evident: the

Fig. 8. Yarn from Z-shaped double crease.

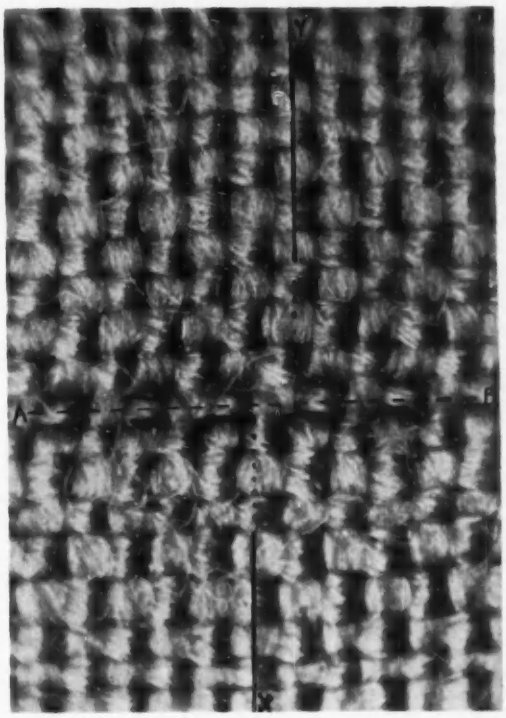

Fig. 9. View into concave face of sharp crease; note dislocation of yarns crossing crease line AB.

crease deformation at b involves bending around a crossing yarn and is of the "pointed" type shown in the upper yarn (A) of Figure 6; immediately adjacent to this crease, at a, crimp loss has occurred; at d, crease curvature is in the opposite direction to the crimp curvature, and lateral and ventral buckling occurs as well as a straightening of the crimp; finally, principal curvatures of this crease occur at the crimps adjacent to the crimp marked d, and this crease is consequently a squared-off type. The presence of two crossing yarns inside crimps c and e and of a crossing yarn at d, outside the blunt end of this squared-off crease, probably is the principal factor in causing the squared-off configuration. However, axial compression of the yarn at the straightened crimp d may possibly contribute to the tendency to curve sharply at points c and e.

In view of some of these observations, it is possible to explain the variation in average maximum fiber strain from yarn to yarn illustrated in Table I. It is believed, now, that yarns 1 and 3 represented the case where the intersecting yarn fell on top of the crease, resulting in a decrease in curvature of the apex crimp concomitant with increase of curvature in the bounding crimps. The curvatures measured here were therefore in the bounding crimps. Yarn 2 would then be a yarn exhibiting the so-called pointed shape, and the curvatures recorded were those resulting from the increased bending of the central crimp. In any case, the quantitative data are presented only for illustration, as work in this area continues.

Gross Fabric Distortion

A distortion not readily detected in single yarns was observed on whole samples of creased fabric. The effect is illustrated in Figure 9, a view into the concave side of a crease running across the warp yarns from A to B.

It will be seen that there is a marked dislocation of the orthogonality of the weave, along the locus of the crease. Note the displacement of line X from line Y, drawn along the same warp yarn. It is proposed that part of the bending strain imposed on the creased yarns is relieved by a tendency for them to twist at the regions of imposed curvature. This tendency is restricted by the intersecting yarns and results in a coordinated lateral thrust and consequent lateral displacement in the plane of the fabric. The distortions of the individual fibers in bent yarns are apparently rather complex, as witness the idealized geometry described by Backer [TEXTILE RESEARCH JOURNAL 22, 668 (1954)].

Manuscript received December 8, 1958.

Adsorption of Labeled Sodium Carboxymethyl Cellulose by Textile Fibers[1]

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Abstract

A carbon-14-labeled sodium carboxymethyl cellulose (CMC) has been employed to measure its adsorption by textile fibers, and in the case of cotton, to investigate the relationship between adsorption and detergency action. Adsorption of CMC by cotton was found to depend on the presence of excess cations in solution, increasing with cation concentration and valence. Equilibrium adsorption of CMC in the presence of excess cations was found to have a zero temperature coefficient. Variation of pH within the alkaline range had no significant effect. Limited measurements with fibers other than cotton indicated little or no adsorption by wool, Orlon,[2] or acetate (in the presence of excess cations). There was significant adsorption by nylon and rayon, but this adsorption was greatly reduced by addition of an alkylaryl sulfonate. Detergency evaluations with the labeled CMC and with unlabeled material indicate that CMC adsorbed on cotton has a significant action in preventing redeposition of particulate soil materials. The adsorption and detergency data indicate that the quantity of CMC required to form a monomolecular layer on cotton fibers may be on the order of 400–500 micrograms per gram of cotton.

Introduction

An important industrial use of sodium carboxymethyl cellulose (CMC) is as an additive to synthetic detergent compositions intended for laundering applications. It is well known that a small percentage of CMC in such formulations is very effective in preventing the redeposition of soil once it has been removed from the substrate. This at least is true when the substrate is cotton fabric. Published information on the performance of CMC with other types of fibers is quite limited, but it is known that the effectiveness of CMC in preventing the deposition of carbon soil on fabric varies greatly with the type of fiber involved [6]. This would indicate that the mechanism by which CMC reduces soil redeposition must involve the fiber surface as well as the soil particles. The specificity of action with regard to fiber types is explained satisfactorily by the commonly held theory that the effectiveness of CMC depends on its adsorption by the fibers. This adsorption by fabric, and probably by soil particles, is presumed to change the surface potentials in such a way as to reduce attraction between fabric and soil. Published data on the adsorption of CMC by cotton have been inconclusive, however, resulting in some uncertainty as to the mechanism involved in the detergency action.

Nieuwenhuis [9, 10, 11] has maintained for some years that the effectiveness of CMC with cotton is due, at least in part, to adsorption by the fibers. He has suggested, on the basis of unpublished experimental data, that CMC is adsorbed in a "loose" form, readily removed by rinsing.[3] Bartholome and Buschmann [1] published some of the first quantitative data on adsorption of CMC by cotton, based on a colorimetric method for determination of CMC in solution. They obtained high adsorption values, in the range of 4000–10,000 micrograms per gram of cotton, at solution concentrations of 0.01–0.05%. Fong and Ward [4], on the basis of electrophoresis and sedimentation measurements, concluded that CMC acts through adsorption on the cotton fibers. From zeta potential measurements, Stackelberg et al. [13] and Stillo and Kolat [19] concluded that CMC is adsorbed on cotton and that this is a factor in detergency action.

[1] Presented at the 134th National Meeting of the American Chemical Society at Chicago, Ill., September 1958.

[2] Du Pont trademark.

[3] Nieuwenhuis and Tan, in a more recent publication (2nd International Congress of Surface Activity, Vol. 4, 1957), propose on the basis of wash test results that CMC is absorbed by bleached cotton but not by unbleached material.

In apparent contradiction to the observations of these investigators is the work published recently by Stüpel [20, 21, 22]. Using a micro technique with acridine orange as a fluorescent indicator for CMC, he has found no indication of CMC adsorption by cotton fibers, while he has observed strong adsorption by various soil materials. He has concluded that adsorption by soil particles is the principal mechanism in the functioning of CMC.

In view of the contradictions regarding the adsorption of CMC by fibers, we undertook several years ago to prepare a labeled CMC of detergency grade in hopes of obtaining more conclusive data on adsorption by fibers and the relation to detergency action. Meanwhile, it has been learned through publications by Stawitz and coworkers [15, 16, 17, 18] that the German workers have been pursuing a very similar line of investigation. Our findings as reported here appear to be in very good agreement with theirs.

Preparation of Labeled CMC

Sodium carboxymethyl cellulose is prepared by the reaction of sodium hydroxide and chloroacetic acid (or sodium chloroacetate) with a suitable cellulose, with the formation of sodium glycolate as a byproduct. As each glucose unit of the cellulose molecule has three hydroxyl groups available for reaction, the maximum theoretical degree of substitution (DS) would be 3.0. This is never reached in practice, and for detergency applications DS generally is less than 1.0.

It was decided to prepare a tagged CMC with degree of substitution of about 0.7, in the medium–low viscosity range, and with a specific activity on the order of 0.5–1.0 millicurie/g. in order to provide adequate sensitivity for adsorption measurements. Since a total of one millicurie of activity was to be used, this involved preparation on a 1-g. scale. Preliminary trials indicated that such a small-scale reaction could be carried out best with a slurry of the flocked cellulose. *n*-Propyl alcohol was selected as a suitable slurry medium. The tag was to be incorporated in the carboxy group, and the initial plan was to use chloroacetic acid-C^{14}. After some difficulty was experienced in obtaining a satisfactory tagged chloroacetic acid, it was decided to use bromoacetic acid-C^{14} instead, since reportedly the latter could be supplied in a purer form.

The procedure was worked out in a number of trial runs until a product with the desired properties could be prepared consistently. The product of each trial run was checked for degree of substitution, active agent content, and detergency properties as determined with a standard carbon soil whiteness retention test.

Procedure

The reaction was carried out in a 100-ml. round-bottom flask, fitted with motor-driven stirrer, thermometer well, and side tube for additions. Materials and quantities used are listed below.

Cellulose, flocked "Soft Kraft" (Weyerhaeuser)	0.99 g.
n-Propyl alcohol (reagent grade)	17.8 g.
Bromoacetic acid-C^{14} (Tracerlab)	0.153 g.
Bromoacetic acid (Eastman)	0.536 g.
Sodium hydroxide (reagent grade)	0.42 g.

The bromoacetic acids and sodium hydroxide were employed as aqueous solutions, which together contributed about four grams of water to the reaction mass.

The tagged bromoacetic as received showed signs of decomposition, presumably due to radiolysis. It was purified by vacuum distillation which produced colorless crystals. Radioassay indicated recovery of essentially 1 mc. of purified material. The inactive bromoacetic acid was used as received, but the amount of acid used was based on titration of a stock solution. The tagged bromoacetic acid was combined with the inactive acid in 1 ml. of solution.

The flocked cellulose and alcohol were first stirred together in the reaction flask for 15 min. at room temperature. The sodium hydroxide solution (2.305 ml.) then was added dropwise over a period of 15 min. and stirring continued for an additional 2 hr. at room temperature. The bromoacetic acid solution was added dropwise over a period of 30 min. at room temperature, with stirring. The temperature then was raised to 70° C. by means of a water bath and stirring continued for 3 hr.

The product was washed free of sodium bromide and sodium glycolate with repeated portions of warm 80% ethyl alcohol and finally washed with absolute ethyl alcohol and dried to constant weight. Total yield of purified and dried CMC-C^{14} was found to be 1.264 g. Radiochemical yield, as determined from radioassays of the bromoacetic acid and of the final product, was 66.6%. Assuming the use of 1 mc. of activity, this indicated a specific activity of about 0.53 millicurie per gram of CMC.

Properties of the Tagged CMC

The tagged CMC was found to be readily soluble, giving clear solutions with very little insoluble material, comparable to a good quality commercial product in these respects. As a further check on the material, determinations were made of degree of substitution, viscosity, and detergency properties.

Degree of substitution was determined by the method of Eyler et al. [3], modified to permit the use of only about 0.02 g. of CMC per determination. Duplicate determinations gave an average value for the DS of 0.71.

Viscosity of a solution of the tagged CMC was determined with a micro capillary-flow apparatus. Although this is not the preferred viscosity method for use with CMC, because of the thixotropic nature of the solution, it was found that with proper control of test conditions reproducible viscosity values could be obtained. Direct comparisons were made between the tagged CMC and solutions of a number of samples of commercial CMC's of known Brookfield viscosities. The tagged material was comparable to a commercial product having a Brookfield viscosity for a 2% solution of about 40 cps, placing it in the medium-low viscosity range.

Detergency action of the tagged CMC was checked by measurements of soil redeposition in comparison with commercial detergency grade CMC's. The tests were made with a miniature wash apparatus previously described [7] using a standard carbon-soiled cloth. Clean and soiled swatches were washed together and redeposition on the clean swatch determined from reflectance measurements. When used in combination with a commercial alkylaryl sulfonate, the tagged CMC was found to be comparable to commercial detergency grade products in preventing soil redeposition.

Adsorption Measurements

Methods

In this work, adsorption measurements have been made in two ways: by direct measurement of activity on cloth or fibers after separation from the solution and by determination of the decrease in CMC concentration in the solution in contact with the cloth or fibers. The first method is preferred when applicable, because of the much greater sensitivity attainable.

In tests in which measurements were made by taking counts on the cloth, the samples were 1-in. discs, cut with a die. Two of these generally were agitated together in 10 ml. of solution in a 50-ml. conical flask. Agitation was by means of a mechanical shaker arrangement, with flasks partly submerged in a water bath for temperature control. With completion of the treatment period, the cloth discs were removed from the solution and rinsed briefly (30 sec.) in two portions of demineralized water at room temperature. Some tests were made also in which the discs were not rinsed, but instead were blotted by being pressed between filter papers and then placed quickly in a weighing bottle. From weights of damp discs and dried discs the amount of retained solution was determined, and an equivalent correction subtracted from the observed counting rate.

Counting was done with an end-window Geiger counter (TGC-2), using a shielded sample changer with fixed geometry. Discs were mounted for counting on 1-in. diameter aluminum supports, with the discs held flat by a thin coating of rubber cement, which was allowed to dry thoroughly before the cloth was pressed lightly in place. It was determined that this method of mounting did not remove any significant amount of activity from the cloth surface in contact with the cement. Generally both sides of a disc were counted.

In order to convert counts taken on cloth discs into amounts of CMC, measurements were made with discs carrying known amounts of CMC, applied in such a way as to be uniformly distributed in the cloth. A CMC solution was applied by means of a micropipette to the center of a cloth disc supported on the points of straight pins. One hundred lambda of solution was found to be a suitable volume, just sufficient to dampen a 1-in. disc. During the drying period the disc was turned over periodically. This procedure was found to give reasonably uniform distribution of material in cloth, as determined by radioautographs. These reference discs were counted under the same conditions as the test discs to determine counts per minute equivalent to one microgram of CMC.

In those tests in which adsorption was determined from change in solution concentration, counts were taken on dried aliquots of the initial and final solutions. Although simple enough in principle, such assays can give difficulty due to variations in distribution and thickness of the residue. The following

procedure, however, was found to give reasonably reproducible results. One-inch squares of glass (cut from microscope slides) were wiped and flamed with a bunsen burner. After they were cooled, a ring of silicone grease was applied by a printing method and the glass warmed again briefly. The measured aliquot of solution was applied within the silicone ring and taken to dryness on a hot plate. The residue then was redissolved in about 10 λ of water, spread uniformly over the defined area with a Teflon splinter, and then dried quickly by warming under vacuum. With care, such assays can be reproduced within about 1%.

Adsorption by Cotton

The cotton cloth used in this work was from a special stock of bleached, unsized Indianhead muslin procured for detergency testing. It was used as received, unless otherwise indicated. CMC solutions were prepared with demineralized water and filtered through glass wool before use.

Initially, trials were made with solutions of the pure CMC, in the absence of additives. When cotton discs were treated for 10 min. at 60° C. in 0.01% CMC-C^{14} solution followed by rinsing in demineralized water, apparent adsorption was found to be on the order of 6 micrograms of CMC per gram of cotton. Similar tests for longer periods at room temperature gave essentially the same results.

To check on the possibility of the CMC being lightly adsorbed and removed by rinsing (as suggested by Nieuwenhuis), some further tests were made with 0.01% CMC solutions in which the cotton discs were blotted after treatment, rather than rinsed, retained solution determined by weight and correction made to the observed count, as previously explained. With treatment periods varying from 5 min. to 16 hr. at room temperature, the maximum apparent adsorption found was 10 micrograms per gram of cotton. Essentially the same results were obtained with blotting as with rinsing, and it was apparent that no significant amount of adsorbed CMC had been removed by rinsing in the previous tests.

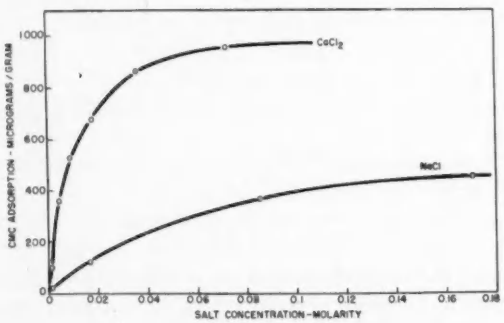

Fig. 1. Effect of cations on adsorption of CMC by cotton. CMC concentration 0.01%, 10 min. treatment at 60° C.

Since these initial trials indicated that adsorption of CMC from solutions of the pure material was relatively insignificant at the low concentrations of interest in connection with detergency use, attention was directed toward the effects of additives. Neither a neutral soap nor a pure alkylaryl sulfonate (salt free) had significant effect on the adsorption of CMC. It was found, however, that addition of an inorganic electrolyte to the CMC solution had a very pronounced effect in increasing CMC adsorption on cotton. Further, this effect of salts was essentially independent of the anion present but varied greatly with the charge on the cation. This is illustrated in Figure 1, showing the effects of varying concentrations of NaCl and $CaCl_2$ on adsorption of CMC by cotton, CMC concentration being held constant at 0.01%.

The data in Figure 1, being for 10-min. treatment periods at 60° C., do not represent equilibrium conditions, but rather are intended to approximate conditions in a detergency operation. Under these conditions, low concentrations of calcium salt have a much greater effect than the same molarity of sodium salt, the difference in adsorption of CMC being on the order of fivefold. At higher concentrations, however, this difference in effects of calcium and sodium decreases and appears to approach a 2-to-1 difference. This might indicate formation of a single molecular layer on cotton in the presence of sodium ions, and a double layer in the presence of calcium ions. Present data are not conclusive on this point, and further measurements under equilibrium conditions would be required.

Trials were made also with magnesium, aluminum, and thorium salts in an effort to obtain further information on the effect of cation charge on adsorption of CMC. The effect of magnesium was found to be about the same as that of calcium. Aluminum sulfate and thorium nitrate, even at very low solution concentrations, precipitated the CMC; no valid adsorption results could be obtained. Addition of alkali (NaOH or NH_4OH) to the aluminum-CMC

TABLE I. Effect of pH on Adsorption of CMC by Cotton: CMC and Sodium Ion Concentrations Held Constant

pH of soln.	CMC adsorption, Microg./g.
1.5	1740
5.0	184
7.1	145
9.0	148
11.3	141

solutions prevented precipitation of CMC, but when such clarified solutions were tested it was found that the complexed aluminum ions had no pronounced effect on the adsorption of CMC by cotton.

Since laundry detergents normally contain one or more alkaline builders, the effects of various types of alkalies on adsorption of CMC by cotton have been investigated to some extent. In the presence of sodium carbonate, tetrasodium pyrophosphate, sodium metasilicate, and trisodium phosphate, adsorption is of the same order as in the presence of a neutral sodium salt giving the same sodium ion concentration. Presence of the various anions had no pronounced effect on adsorption.

The effect of pH was investigated further by determining adsorption of CMC over the pH range from 1.5 to 11.3 (as determined with the glass electrode at 25° C.). CMC and sodium ion concentrations were held constant at 0.01% and 0.02 *N* respectively. Adsorption values as obtained with 10-min. treatment periods at 60° C. are given in Table I. It is apparent that variations in pH within the alkaline range had no significant effect. The large apparent increase in adsorption at low pH might be due in part to a hydrogen ion effect, but there probably is precipitation of acid CMC on the fibers at pH 1.5, although precipitate was not visible in the solution at this low CMC concentration.

The rate of adsorption of CMC at 60° C. from a solution containing 0.15% sodium sulfate and 0.01% CMC is indicated by Figure 2, in which each point represents the average value for four cotton discs treated continuously for the indicated time. Although initial adsorption is rapid, with 50% of the maximum being reached in about 4 min., equilibrium requires about 2 hr. Limited measurements at 25° C. indicate that, while adsorption is considerably slower at the lower temperature, the same equilibrium value is reached in time. Measurements to date indicate a zero temperature coefficient for equilibrium adsorption.

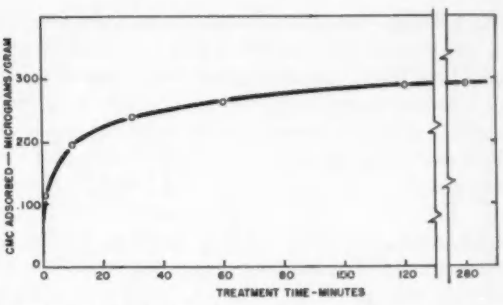

Fig. 2. Rate of adsorption at 60° C. Solution contains 0.01% CMC and 0.15% Na_2SO_4.

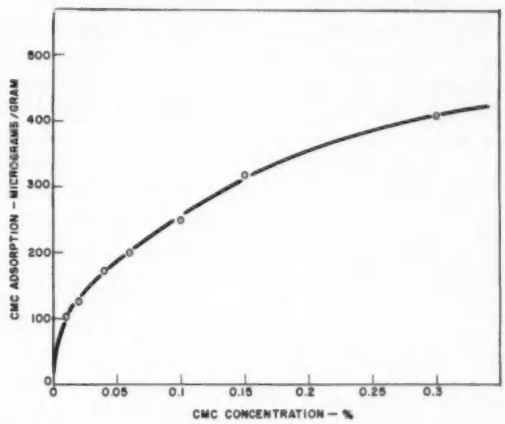

Fig. 3. Effect of CMC concentration on adsorption by cotton; solutions contain 0.25% KREELON 4D, 10 min. treatment at 60° C.

Although equilibrium isotherms for adsorption of CMC in the presence of excess cations have not been determined, some information on effect of variation in CMC concentration with a treatment time of 10 min. at 60° C. is given in Figure 3. These tests were run with solutions containing 0.25% of a commercial alkylaryl sulfonate containing 60% sodium sulfate (KREELON 4D), intended primarily to provide data for possible correlation with detergency results. Although this curve was not extended to sufficiently high concentrations to show a definite plateau, it appears to be approaching a maximum in the region of 400–500 microg./g. This is about the same maximum adsorption as that obtained with increasing sodium ion concentration (Figure 1).

The adsorption results presented so far have been based on counts taken directly on cotton discs after rinsing and drying, this being the most convenient

and sensitive method of measurement. As a means of verifying values obtained in this way, comparisons have been made in several cases with values obtained by solution assays (to determine change in concentration) and with values obtained by taking counts on discs that were blotted, rather than rinsed, with determination of retained solution by weight. Generally, the three methods have given essentially the same results, provided there is sufficient change in concentration to permit accurate determination by solution assay. As an example, when cotton discs were treated for 10 min. at 60° C. in solution containing 0.01% CMC and 0.1% calcium chloride, the value obtained from counts on rinsed discs was 593 microg./g., as compared with 603 by solution assay and 563 by counts on blotted discs. These results indicate that no large error results from removal of adsorbed CMC by rinsing and that the method for converting counts per minute on the cloth to quantity of CMC is reasonably valid.

A number of tests have been made also in which chopped cotton fibers (prepared from the Indianhead muslin) have been used in place of cotton discs, with determination of adsorption from solution assays and from counts taken on the rinsed fibers. Results were comparable to those obtained with discs, with no indication of significant increase in adsorption due to more intimate contact between solution and fibers.

Adsorption by Fibers Other Than Cotton

A limited amount of work has been done with wool, nylon, Orlon, rayon, and acetate in order to determine whether significant amounts of CMC would be adsorbed at the low concentrations encountered in detergency use. All of these tests were run at 60° C. with sodium sulfate or commercial alkylaryl sulfonate (60% sodium sulfate) as additives to the tagged CMC solutions.

Since the fabrics were obtained from retail sources in a variety of weights and weaves, the tests were run with chopped fibers so that results would be more comparable, with supplementary tests in some cases with cloth discs. The chopped fibers were prepared with a Wiley mill and were water washed and classified to remove powdery fines. The fibers then were washed in three portions each of ethyl alcohol, ethyl ether, and carbon tetrachloride and dried thoroughly before use.

The adsorption tests were run with 1 g. of fibers in 20 ml. of solution containing 0.005% tagged CMC and 0.25% of commercial alkylaryl sulfonate or 0.15% sodium sulfate. Treatment periods were for 4 hr. at 60° C. Solution assays were taken before and after treatment; counts were taken also on aliquots of the rinsed and dried fibers.

The tests with CMC-alkylaryl sulfonate-sodium sulfate solutions indicated no significant adsorption by wool, Orlon, rayon, or acetate. There was a slight apparent adsorption by nylon, on the order of 16 microg./g.

With CMC-sodium sulfate solution, there was no significant adsorption by wool or acetate. There was significant adsorption by nylon (about 125 microg./g.) and by rayon (about 60 microg./g.). Apparently there is some adsorption of CMC on nylon and rayon in the presence of excess cations, but this is greatly decreased by addition of alkylaryl sulfonate.

Detergency Effect of Adsorbed CMC

In an effort to demonstrate a direct relation between the adsorption of CMC by cotton and the detergency effect, soil redeposition measurements have been made using several test soils. These have included a C^{14}-tagged carbon black-Nujol soil applied to cloth by rubbing [7], a Ca^{45}-tagged clay soil applied to cloth in aqueous suspension, and a conventional type inactive carbon black soil on cotton [24]. The clay soil, which has not been described previously, was prepared by labeling a montmorillonite type clay with Ca^{45} by exchange, fixing the tag by firing to 1000° C., grinding, washing, and water-classifying for 1 hr. Resulting particle size was on the order of 0.05–0.10μ.

Wash tests were run with a miniature washer described previously [7]. Two cloth discs, one soiled and one clean, were washed together and soil redeposition determined from measurements on the initially clean disc. When inactive carbon black soil was used, redeposition was determined by reflectance measurement, using a Photovolt reflectometer. When tagged soils were used, redepositions generally were determined from direct counts taken on the cloth, except when both C^{14} and Ca^{45} activity were present, in which case a combustion procedure was used to remove the carbon activity, permitting determination of Ca^{45} activity in the ash. All wash tests were run at 60° C. in solutions prepared with demineralized water.

In Figure 4 a comparison is made between adsorp-

TABLE II. Effect on Carbon Soil Redeposition of CMC Preadsorbed on Cotton

Pretreatment of cloth	Reflectance after washing, %
None	65
$CaCl_2$ solution (0.05%)	67
Tagged CMC–$CaCl_2$	77
Regular CMC–$CaCl_2$	77

tion of CMC by cotton and redeposition of the tagged carbon and clay soils with variation of CMC concentration in a 0.25% solution of commercial alkylaryl sulfonate (KREELON 4D). Soil redeposition values have been stated on an arbitrary scale of 100, based on redeposition from a 0.25% solution of KREELON 4D containing no CMC. Since the adsorption data were obtained with the tagged CMC, while redeposition measurements were made with an inactive CMC of similar properties, there is no assurance that actual adsorption from the solution of inactive CMC would follow the curve shown. The mirror image relationship of the curves, however, might be taken to indicate some relation between increase in CMC adsorption and decrease in soil redeposition. The fact that carbon soil and clay soil redeposition values tend to follow the same curve is largely fortuitous, and would not necessarily apply with other types of carbon and clay soil. We have found that the particular shape of the soil redeposition curve depends on the particle size distribution of the soil.

As a means of isolating the effect of CMC adsorbed on the cloth from any effect of CMC in solution, a number of tests were made in which CMC was preadsorbed on cotton discs, which then were used as the clean cloth in soil redeposition measurements. The general procedure was to pretreat the clean cotton discs in CMC-$CaCl_2$ solutions at 60° C. to give a known level of adsorbed CMC. The discs then were rinsed thoroughly, dried, and used for soil redeposition measurements in KREELON 4D solutions. Comparisons were made with untreated, clean discs and with discs that were pretreated in $CaCl_2$ solution without CMC. It was determined that in the washing operation 10–15% of the adsorbed CMC was removed from a pretreated cloth disc, producing on the order of 0.0001% CMC in solution. This amount of CMC in solution has been found to have a negligible detergency effect.

By use of the inactive carbon black soil, tests of this type were made in which the clean discs were pretreated with the tagged CMC and also with a detergency grade commercial CMC, both at 0.01% in combination with 0.05% $CaCl_2$. Pretreatment for 10 min. at 60° C. resulted in adsorbed CMC on the order of 360 microg./g. in the case of the tagged CMC and presumably of the same order with the commercial product. Results of the wash tests are given in Table II.

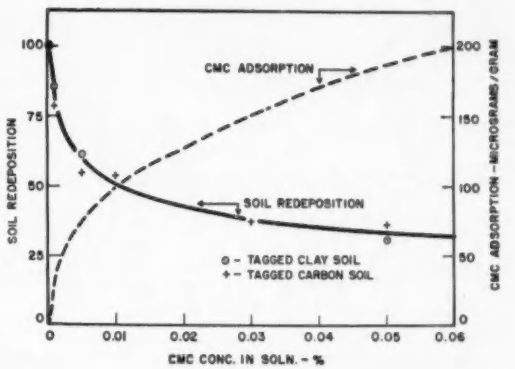

Fig. 4. Soil redeposition and CMC adsorption by cotton cloth as functions of CMC concentration in solution of KREELON 4D alkylaryl sulfonate (adsorption determined with labeled CMC, soil redeposition determined in the presence of unlabeled CMC).

Effect of the preadsorbed CMC is quite pronounced, amounting to a 12% improvement in reflectance, representing a considerable difference in appearance. For comparison, initial reflectance of the clean cotton cloth was about 82%. Pretreatment of cloth in $CaCl_2$ solution without CMC had a slight but not very significant effect on redeposition.

Similar tests were made in which the clean cotton discs were pretreated with 0.01% regular (untagged) CMC plus 0.05% $CaCl_2$; after being rinsed and dried, they were washed with discs soiled with the tagged clay soil. With this soil also, preadsorbed CMC caused a pronounced decrease in soil redeposition, to about one third of that found on untreated discs. Increasing the $CaCl_2$ concentration in the pretreatment solution so as to increase the adsorption of CMC was found to have no additional effect in reducing soil redeposition—that is, the adsorbed CMC appeared to reach a maximum effectiveness in the region of 400 microg./g., assuming that adsorption of the unlabeled CMC was approximately the same as that determined with the labeled material under the same conditions.

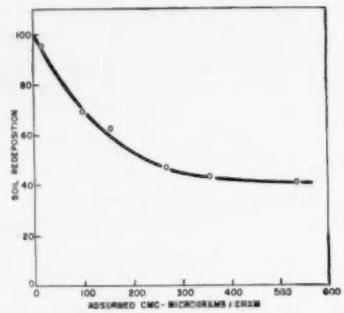

Fig. 5. Tagged clay soil redeposition on cotton cloth pretreated to give varying levels of adsorbed CMC-C^{14} (washed in 0.25% KREELON 4D solution).

Since the actual adsorption on discs pretreated with the unlabeled CMC was not known, additional tests were made in which discs were pretreated with tagged CMC solutions, with variation in $CaCl_2$ concentration to give a range of adsorptions. Soil redeposition measurements then were made with the tagged clay soil. In this case, the cloth discs were ashed to obtain the final count on redeposited clay soil, as explained previously. The soil redeposition values vs. measured CMC adsorption are given in Figure 5. These results are in agreement with those obtained in the equivalent tests with unlabeled CMC. A maximum effect of the preadsorbed CMC is reached between 400 and 500 microg./g., perhaps indicating the formation of a complete monomolecular layer in that region.

Discussion

Although our studies on adsorption of CMC from solutions of the pure material were quite limited in scope, our results are in agreement with those of Stawitz, Klaus, and Krämer [16], and it is apparent that the type of CMC studied is not adsorbed on cotton in significant amounts from solutions of the pure material at low concentrations. There is no apparent explanation for the very high adsorption values found by Bartholome and Buschmann [1], who presumably also were working with solutions of pure material.

Adsorption on cotton of CMC in the presence of excess cations would appear to be well established by these radiotracer measurements supported by the observed effects of preadsorbed CMC on soil redeposition. The fact that Stüpel [20, 21, 22] has been unable to detect the presence of adsorbed CMC on cotton fibers under comparable conditions perhaps indicates that the quantity involved is below the sensitivity limit of his fluorescent indicator method.

The quantities of CMC adsorbed by cotton under the conditions studied are relatively small in comparison with values for adsorption of some other materials by cotton. According to data cited by Harris [5], adsorption values for soaps on cotton are on the order of ten times as great. In considering the possible detergency effect of the observed values for CMC adsorption, it is of interest to consider what they might constitute in terms of a molecular layer. The quantity of CMC required to form a molecular layer on cotton fibers cannot be estimated accurately because of very large uncertainties regarding the specific surface of the cotton fibers available for adsorption of CMC molecules. If one based the estimate on the surface areas of swollen cotton as determined by nitrogen adsorption measurements, amounting to about 2×10^6 cm.^{2}/g. [14], it would be found that the observed adsorption values amounted to a very small fraction of the estimated molecular layer. It is evident, however, that such an estimate could be very misleading, since the "inner" surfaces of cotton accessible to nitrogen molecules would not be accessible to the large CMC molecules, which might be expected to bridge over many of the irregularities in the fiber surface. It seems more reasonable to estimate a minimum value for a molecular layer, based on values for the outer surface of cotton fibers. Sullivan and Hertel [23] give values of $2.3\text{–}3.2 \times 10^3$ cm.^{2}/g. of cotton as determined from microscopic measurements of fibers. Assuming the lower of these values, and taking 100 Å^2 as a rough estimate of the area occupied by each substituted cellobiose unit in the cellulose molecule (based on dimensions given by McBain [8]) with a corresponding molecular weight of 438 per unit, a minimum value for a monomolecular layer of adsorbed CMC would be

$$\frac{2.3 \times 10^3 \text{ cm.}^2\text{/g.} \times 438 \times 10^6}{100 \text{ Å}^2 \times 10^{-16} \text{ cm.}^2\text{/Å}^2 \times 6.02 \times 10^{23}} = 167 \text{ microg./g. cotton}$$

The actual value for a molecular layer no doubt would be higher than this minimum estimate. Actual specific surface available for adsorption should be greater than the value used due to swelling of the fibers. Further, effective surface area for a CMC

molecule could be less than the sum of the areas of the substituted cellobiose units if there were a tendency for the chains to fold or coil [2]. We would suggest that the actual value for a molecular layer for the particular CMC and cotton used in these studies falls in the region of 400–500 micrograms per gram of cotton. This is indicated by the tendency for adsorption (in the presence of monovalent cations) to reach a maximum in this region, and also by the observation that this quantity of preadsorbed CMC had a maximum effect in preventing soil redeposition.

Although it has not been proven that adsorption of CMC on cotton is the only mechanism involved in its detergency action, comparisons of the effectiveness of preadsorbed CMC and of CMC in the detergent solution would seem to indicate that adsorption on the fibers is at least an important factor. Assuming that the effectiveness of CMC does in fact depend on adsorption by the fibers, which in turn depends on the presence of excess cations, it might be thought that a relationship between the effectiveness of CMC and the presence of inorganic electrolytes could have been deduced from the results of numerous laboratory and field studies of the detergency action of CMC. There have been indications of this, but the relation has been obscured by the independent action of electrolytes in promoting the deposition of soil on fabric. As in the case of CMC adsorption, the effect of electrolytes on soil deposition depends on the charge on the cation, the effect being much greater with calcium than with sodium [12]. Addition of electrolyte to a detergency system, then, tends to increase the deposition of soil, but at the same time increases the adsorption of any CMC present. In practice, the beneficial effect on CMC adsorption more than counteracts the adverse effect of increasing soil deposition.

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Characteristics and Rate of Wear of Worsted Serge in Trousers

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Abstract

The performance of a worsted serge in drycleaning and as trousers was studied. A 58's grade domestic wool was woven into a 13-oz. serge (standard 2/2 twill, 68 × 68) that was dyed gray. Fifty-four pairs of trousers were worn by college men for one, two, or three academic years (11, 22, or 33 weeks). Breaking strength was determined and microscopic examination of yarns for percentage of worn fiber ends was made in three locations of anticipated heavy wear—waist front, knee, and seat. Loss in strength was related to time in service. The rate of deterioration was greater during the second and third years than during the first, and greater for the filling than for the warp. The seat was the most severely worn area. The trousers gave satisfactory performance through the three years. Bursting strength and abrasion resistance were determined in parts where less wear was visible. After the third year, deterioration had advanced to an 18% loss in bursting strength and a 23% loss in resistance to abrasion, and air permeability increased to approximately double its original value. Drycleaning alone had little or no effect on the appearance or the physical properties of the swatches of serge which were cleaned in the same load with the trousers.

THE purpose of this research was to determine the characteristics and rate of wear of a serge fabric manufactured from 58's grade wool of known genetic origin. The worsted material was made into trousers that were worn by college men during one, two, or three academic years. This investigation of performance in end use of an apparel textile included periodic evaluation of appearance and measurement of physical properties as a basis for determining the rate of deterioration of the fabric during wear and drycleaning.

Materials and Methods

Fiber, Fabric, and Garments

The 58's grade wool was clipped from Targhee sheep grown at the U. S. Sheep Experiment Station, Dubois, Idaho. The Forstmann Woolen Company spun this wool into 2/40 worsted yarn for both the warp and filling. The 1/40 component of the yarn had 13.7 turns/in., Z twist, and the 2-ply yarn had 12.7 turns/in., S twist. A 13-oz. serge (a standard 2/2 twill) was woven [4]. The fabric was washed, dyed gray with metachrome dye, sheared, and decated. The texture of the finished serge was 68 × 68.

Fifty-four pairs of trousers were tailored from the serge. The manufacturer used his pattern for cadet uniform trousers; the design had no waistline pleats. Thus, the trousers were a snug fit.

Conditions of service. The trousers were put into service through the cooperation of volunteers from the students at Gallaudet College, Washington, D. C. Each winter different students wore the trousers. Although wearers were selected who were average in respect to size, at some time nearly all the trousers needed slight alterations in waist and length of inseam. Two pairs, to be worn on alternate weeks during a school year, were issued to each participating student, who recorded the number of hours his trousers were in service. A student assistant examined the trousers each week for necessary repairs. The men were asked to wear a pair of trousers for 70 hr. a week, after which the garments were dry-

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cleaned by a commercial plant following its usual method. Nine control pieces of serge, approximately 40 × 56 in., were drycleaned and pressed with the trousers.

Sampling

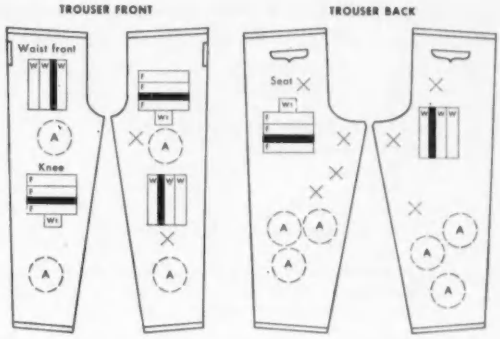
At the end of each year, trousers were withdrawn from service—18 pairs after 11 weeks of wear and 11 drycleanings, 18 after 22 weeks and 22 drycleanings, and 18 after 33 weeks and 33 drycleanings. At these same intervals three pieces of control fabric, drycleaned and pressed, were withdrawn.

Specimens for the determination of physical properties of the trousers were cut from three selected areas of anticipated heavy wear: waist front, 3–5 in. below the waistband; knee, at the approximate bend of the knee; and seat, about 8–10 in. below the waistband. Before any specimens were cut, one air permeability determination was made on each pair at the three locations. Then, warp and filling breaking strength strips and one square for the determination of weight (Figure 1) were cut from each area. Nine trousers were cut according to Figure 1 and the other nine according to a mirror image of that figure. Afterwards, contiguous areas were sampled for bursting strength and abrasion resistance. The approximate location for these latter two tests are indicated in Figure 1 by the dotted circles (abrasion) and ×'s (bursting strength). It will be noted that these are less worn parts than were sampled for breaking strength. For microscopic examination of damaged fibers, ½-in. strips were cut between the breaking strength specimens (Figure 1, shaded areas) from three pairs selected at random from the 18 pairs.

Test Procedures

Raveled-strip breaking strength, count, weight, and thickness (at 0.1 lb./in.^{2} pressure) were determined according to A.S.T.M. D 39–49 [1]. Air permeability, determined by A.S.T.M. D 737–46 [1], was expressed in cubic feet of air per minute per square foot of fabric at 0.5 in. water. Bursting strength was determined by Federal Specifications Method 6122 [2].

For abrasion resistance the inflated diaphragm test described in A.S.T.M. D 1175–51T [1] was followed by using a ½-lb. load on the abradant plate and 4-lb. diaphragm pressure. Specimens were abraded multidirectionally with No. 0 emory paper to the automatic end point.



Empirical Equations for Curves

Warp

Waist front	$S = 51 - 5\frac{1}{2}t + 2t^2 - \frac{2}{3}t^3$
Knee	$S = 51 - 4\frac{1}{2}t + \frac{1}{2}t^2 - \frac{1}{6}t^3$
Seat	$S = 51 - 4\frac{5}{6}t + 1\frac{1}{2}t^2 - \frac{2}{3}t^3$

Filling

Waist front	$S = 48 - 5\frac{5}{6}t + 4\frac{1}{2}t^2 - 1\frac{2}{3}t^3$
Knee	$S = 48 - 6\frac{2}{3}t + 1\frac{1}{2}t^2 + \frac{1}{6}t^3$
Seat	$S = 48 - 10\frac{1}{2}t - 2t^2 - \frac{2}{3}t^3$

Fig. 1. Sampling plan for trousers. Specimens are designated by warp (W) and filling (F) breaking strength, weight (Wt.), abrasion (A), bursting strength (×), and percentage of worn fiber ends by microscopic examination (shaded strips). Air permeability was determined in waist front, knee, and seat areas before specimens were cut.

To measure shrinkage in drycleaning, the specimens (40 × 56 in.) were laid out without tension on a flat, hard surface. Three distances each 30 in. in the warp direction and three distances each 50 in. in the filling direction were marked off. The drycleaned swatches were laid out without tension and the marked-off distances were measured and averaged. Shrinkage in the warp and filling directions, calculated separately, was expressed as percentage.

For microscopic examination, six of the 2-ply yarns, three each of warp and filling, were removed from each selected pair of trousers and separated in the twist counter to give two single yarns. A sample of the single yarn was placed in the twist counter with the clamps set 1 in. apart and the 1 in. was untwisted, cut out, mounted in water on a slide, teased apart, and covered with a cover glass. The whole area of the sample was surveyed for the number and type of fiber ends as described by Macormac and Richardson [3].

TABLE I. Physical Properties of New Serge and of Trousers Worn 1, 2, and 3 School Years

Property	New fabric	Worn trousers*		
		1 year	2 years	3 years
In 3 selected areas of anticipated heavy wear				
Breaking strength, lb.				
Warp	51	47	42	36
Filling	48	41	34	21
Weight, oz./sq. yd.	8.2	8.0	7.8	7.5
Air permeability, ft.³/min./ft.²	44	54	57	79
In less worn areas contiguous to heavy wear				
Bursting strength, lb.	135	125	118	111
Abrasion resistance, cycles	841	737	698	648

* Wear in 1 year represents 11 weeks; 2 years, 22 weeks; 3 years, 33 weeks. Drycleaning was done after each week of wear.

Results and Discussion

Physical Properties of Trousers After Wear

Data on the physical properties of the trousers sampled at the end of each school year following 11, 22, and 33 weeks of wear are reported in Table I.

Breaking strength. During the three school years, the average warp breaking strength of the trousers decreased from 51 to 47, 42, and 36 lb., respectively (8%, 18%, and 29% loss). Decreases in average filling breaking strength occurred during the same periods, from 48 to 41, 34, and 21 lb. (15%, 29%, and 56% loss).

Differences among the three sampling areas (knee, seat, and waist front) are illustrated graphically in Figure 2 with empirical equations which show the relation of change in breaking strength to length of wear. Deterioration increased rapidly with the increasing wear and was more rapid in the filling than in the warp direction.

Coefficients of variation were calculated for the values in the three designated areas. In the warp direction, after the first year the means in the three areas were approximately equal and therefore failed to distinguish among them as to degree of wear. There were only slight differences among the coefficients of variation. After the second year the means of the three areas were again approximately equal, but the coefficients of variation had increased over those of the first year and were larger between the areas. After the third year the considerably larger coefficients of variation indicated the lessening uniformity among the individual readings of strength within an area caused by unevenness of wear. For example, the coefficient of variation for the warp breaking strength was 4.5% in new fabric and 24.0% in the seat area of trousers after three years of wear.

In the filling direction, the mean breaking strength of the knee and seat were approximately the same at any sampling interval; the waist front retained its strength to a greater degree. The coefficients of variation for each area were greater at each successive sampling period. The large coefficients of variation are indications of the lower uniformity in fabric strength of the three strips in an area. With increasing wear, the variability among the strength of the strips increased. For example, the coefficient of variation for the original filling breaking strength had been 6.4%, but after three years of wear the coefficient for the values in the seat area was 35.5%.

Weight. The average weight per square yard decreased at each sampling. By the end of the third year, the weight in the seat area had dropped from 8.2 oz. (original fabric) to 7.2 oz.—a 12% loss; the knee area, however, had lost only 5%. A weight loss of 12% might indicate a critical difference in the actual in-service performance of similar serge.

Air permeability. Air permeability increased considerably after the first year of wear, showed relatively little change in the next interval, but was approximately double the original value after three years (Table I).

Bursting strength. Bursting strength data, from parts where less wear was visible or the fabric looked almost as good as new, are shown in Table I. A decrease of 10 and 17 lb. (7% and 13% loss) was found in the trousers worn one and two years. In the trousers sampled after the third year, the values for bursting strength show that even in these rela-

tively unworn parts, deterioration had advanced to an 18% loss (a decrease of 24 lb.). The coefficient of variation of the bursting strength values for the original serge was 2.2%, which indicated a very high degree of uniformity among the values for the 60 determinations. The coefficient of variation for the 162 values of the 18 trousers worn three years, however, had increased to 11.2%, indicating that the values, although fairly uniform, included a few extremes. Despite these few extreme values, the bursting strength values were more uniform than had been expected. The distribution of the bursting strength per sampling is presented in Figure 3.

Abrasion resistance. As expected in abrasion test results, the variation among the specimens was great. In the new fabric, the number of cycles necessary to produce the automatic end point was 841. The variability among the specimens cut from the new serge was apparent in the range in values (631–1151 cycles). The coefficient of variation was 13.6% for these 60 specimens.

In the relatively unworn parts of trousers, the number of cycles to end point was 737, 698, and 648 after one, two, and three years respectively (Table I). Again, there was a wide range from low to high values in the cycles to the automatic end point, as the correspondingly large coefficients of variation indicated. At the end of the third year, for example, the coefficient of variation was 13.6%—the same as for the new fabric. Therefore, under the procedure of abrasion testing used, the variability among specimens cut from trousers could not be attributed to unevenness of wear occurring in the areas sampled.

Worn fiber ends. Microscopic examination of yarns removed from nine selected trousers showed

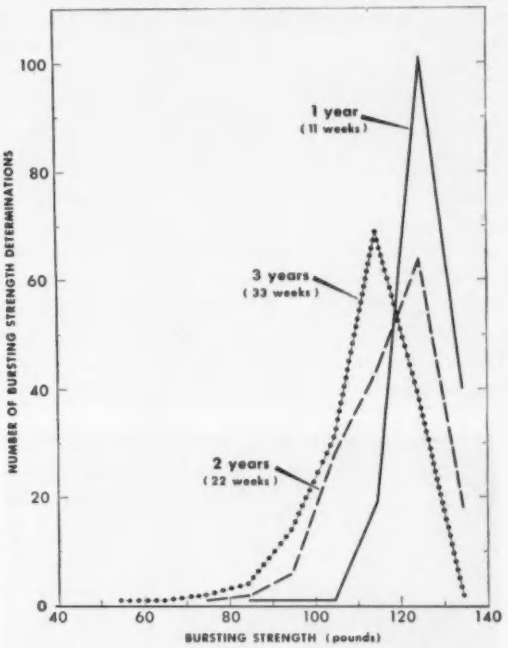


Fig. 3. Distribution of bursting strength determinations on trousers worn for 1, 2, or 3 school years representing 11, 22, or 33 weeks and 11, 22, or 33 drycleanings. These determinations were made in less worn areas than were breaking strength determinations.

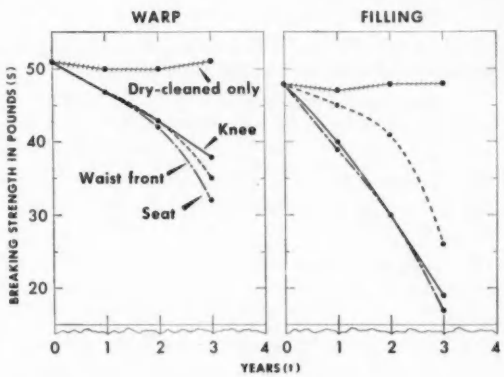


Fig. 2. The relation of warp and filling breaking strength of three areas of trousers to 1, 2, and 3 school years representing 11, 22, or 33 weeks of wear. The "drycleaned only" values are from swatches of serge that were drycleaned together with the trousers 11, 22, or 33 times.

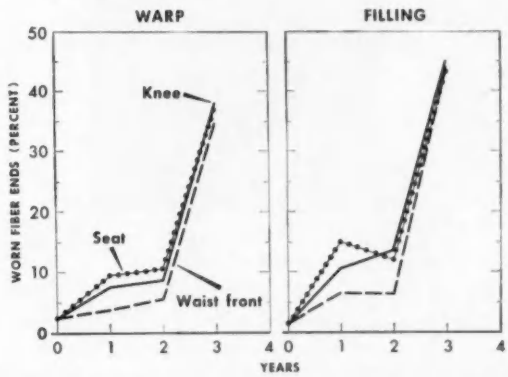


Fig. 4. The relation of worn fiber ends in yarns to length of wear. The yarns were removed from 3 of 18 trousers withdrawn after 1, 2, or 3 school years representing 11, 22, or 33 weeks of wear and 11, 22, or 33 drycleanings.

that in general as the length of wear increased, there was an increasing percentage of worn fiber ends in the yarns; the percentage increased rapidly during the third year (Figure 4). These findings agreed with the breaking strength results that the filling yarns were more damaged than the warp and that the knee and seat were more severely worn than the waist front.

Effect of Drycleaning

The control pieces of serge which had been drycleaned and pressed showed little or no change in count, weight, breaking strength, thickness, air permeability, or bursting strength (Table II). Warp and filling breaking strength has been plotted in Figure 2 for comparison with the strength of worn garments sampled after one, two, and three years. The amount of shrinkage in the filling direction was nominal, 1%, even after 33 drycleanings. Although there was progressive shrinkage in the warp direction, the shrinkage was only 3% after 33 drycleanings.

Fig. 5a. A worn crotch area. Bursting strength determinations in the two thin spots showed losses of 52% and 65%.

Appearance of Trousers

At the end of the third year, the seat of the trousers appeared to be the most worn; differences between waist front and knee could not be differentiated by merely looking down at the garments. By this time the trousers exhibited moderate and severe wear and their general appearance failed to meet the students' standards for classroom clothing.

Figures 5a through 5d show photographs that were made of worn areas of trousers. These selected spots display similar degrees of thinness; however, the extent and shape of these spots varied among individual trousers. The breakdown of the fabric by gradual but continued wear on localized areas was apparent in the thin and threadbare spots and holes.

Summary

The characteristics and rate of wear of 58's grade wool when utilized in a 13-oz. worsted serge has been determined from 54 pairs of trousers worn by college students. The wool, clipped from Targhee sheep, was woven in a standard 2/2 twill with a 68 × 68 texture and dyed gray.

Selected physical properties of the serge after three different intervals of wear were determined. As a criterion of damage occurring in service, the decrease in breaking strength after one, two, and

TABLE II. Physical Properties of Unworn Serge Fabric Before and After 11, 22, and 33 Drycleanings

Property	Number of drycleanings			
	0	11	22	33
Count				
Warp	68	66	67	69
Filling	68	66	69	70
Weight, oz./sq. yd.	8.2	7.9	8.3	8.4
Thickness, in.*	.031	.036	.032	.032
Breaking strength, lb.				
Warp	51	50	50	51
Filling	48	47	48	48
Bursting strength, lb.	135	138	137	136
Air permeability, ft.³/min./ft.²	44	47	48	46
Shrinkage in drycleaning, %				
Warp		1.1	2.7	3.2
Filling		†	†	1.1

* At 0.1 lb./in.² pressure.
† Less than 1%.

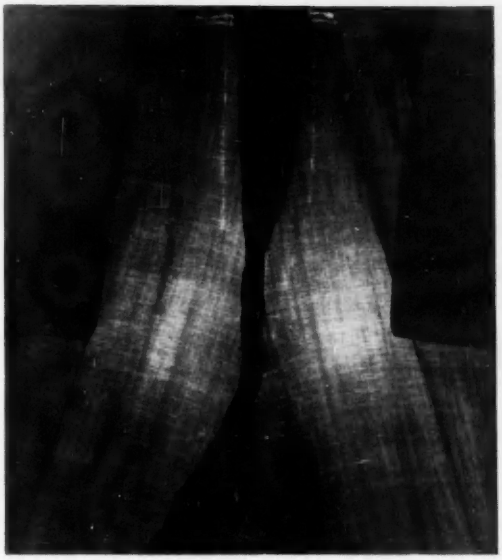


Fig. 5b. Back of trousers, with worn seat and needle damage along the altered back rise seam and belt loop.

Fig. 5c. Trouser front. Waist front area had lost 49% of the warp breaking strength.

three school years (11, 22, and 33 weeks) was measured for three areas of the trousers: waist front, knee, and seat. In 18 trousers worn for three years, the average warp strength of the three areas, which was 51 lb. in the new fabric, had decreased to 36 lb. (29% loss); the average filling strength decreased from 48 to 21 lb. (56% loss). The rate of deterioration was greater in the filling direction than in the warp of the worn trousers and was greater during the second and third years than during the first.

Air permeability, weight per square yard, bursting strength, and abrasion resistance also reflected that changes occurred during service.

Microscopic examination of yarns from nine selected trousers showed that as the length of wear increased, there was generally an increasing percentage of worn fiber ends; the percentage increased rapidly after the second year. The filling yarns contained more damaged fiber ends than the warp yarns. The knee and the seat contained more damaged fiber ends than the waist front. These results agreed substantially with the results from the breaking strength determinations.

Drycleaning alone had little or no effect on the appearance of this serge, and any changes in physical properties were small enough to be considered negligible.

Fig. 5d. Thigh-knee area of trousers.

Under the conditions of wear occurring during the day-to-day living of college students, the trousers gave satisfactory performance when worn for 33 weeks over three school years. After the third year the trousers exhibited moderate and severe wear and their general appearance failed to meet the students' standards for classroom clothing. The breakdown

of the serge in localized areas was characteristic of the wear pattern in all trousers.

Acknowledgments

The authors wish to acknowledge the contributions of the many students, technicians, and administrators who cooperated in this study. Special appreciation is expressed to Alfred R. Macormac for microscopic analysis and to Hazel M. Fletcher for valuable suggestions regarding treatment of the data.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Method Used for Determining Warp Crimp

Southern Utilization Research
and Development Division [1]
1100 Robert E. Lee Boulevard
New Orleans, Louisiana
January 27, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In studying the characteristics and properties of various types of cotton fibers, yarn crimp is an important factor that is very difficult to determine accurately from warp yarns removed from the fabric. Crimp, as we consider it, is the percent contraction of the yarn in the fabric due to the interlacing of warp and filling in weaving. The accurate determination of crimp is of considerable importance to the manufacturer in the weaving of new style cloths and/or patterns as well as to the research worker in the development of new fabrics, since crimp has a marked influence on the strength, abrasive resistance, tear resistance, texture, and flexibility of fabrics [1].

In order to facilitate determining the percent crimp of warp yarn in cloth, a device was developed to accurately measure an 18-in. length of warp yarn pulled from the loom beam in weaving.

The measuring device is shown in Figures 1 and 2 and consists principally of a hardwood wheel A $2\frac{3}{16}$ in. thick and exactly 18 in. in circumference. This wheel was shellacked and the face or outside circumference was sprinkled with 180 Grit silicon carbide grain to provide traction when turning with the warp. The wheel was then mounted in a $\frac{3}{4}$-in.

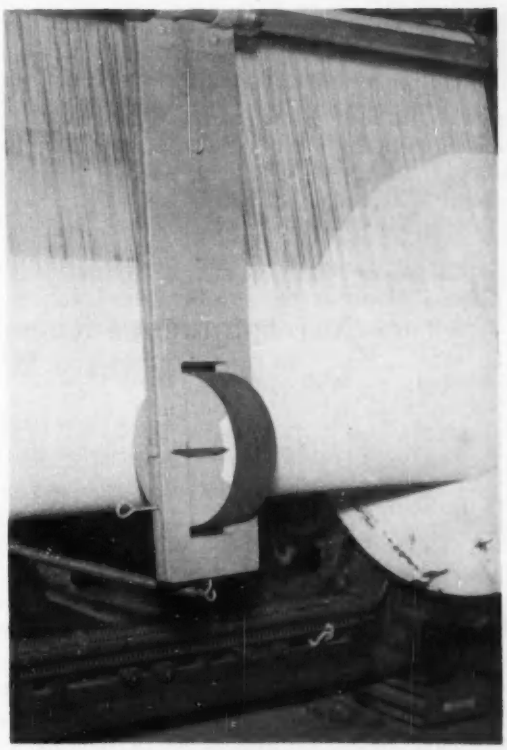

Fig. 1.

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

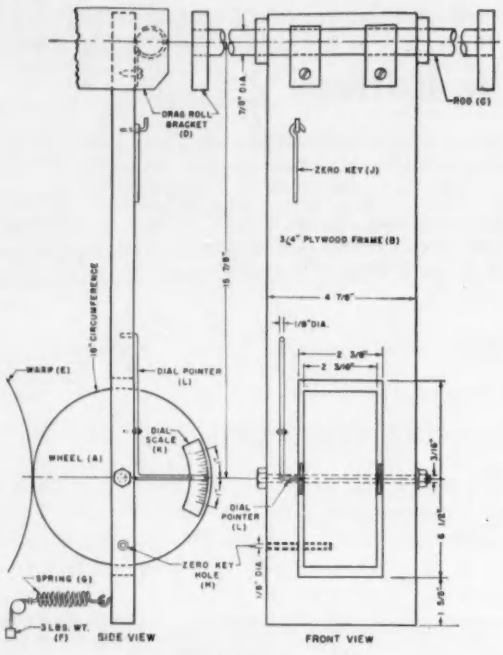

Fig. 2.

plywood frame B that was fastened to a rod C extending between the drag roll brackets D. The wheel is held firmly against the warp E by a 3-lb. weight F suspended beneath the loom and fastened to the measuring device frame by means of a rope and spring connection G to prevent bouncing due to the rocking motion of the loom.

A "zero keyhole" was bored through the frame and into the wheel for accurately setting the wheel with "key" J at the start of the measurement and to mark the end of the measurement. The key is made from a piece of $\frac{1}{8}$-in. diameter rod. Readings can be made at exactly 18 in. by using the key or 18 ± 1 in. in $\frac{1}{16}$-in. increments from scale K marked off on the side of the wheel by reading at pointer L.

In using this device as an aid in determining crimp, the following procedure has been adopted.

1. Insert one pick of filling of a different color from that used in fabric being woven.
2. Set the measuring wheel on zero.
3. Start the loom and weave until measuring wheel comes back to zero.
4. Insert one pick of filling as in Step 1 above.
5. Start the loom and continue normal weaving.

When the cloth is removed from the loom the distance between the two colored picks of filling can be measured; from these measurements the percent crimp can be readily calculated. We believe this method of determining crimp is far more accurate than other methods commonly used.

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E. C. KINGSBERY
N. P. RODDY

Correspondence Regarding "Moisture Regain of Tightly Woven Fabrics"

Shawinigan Resins Corporation
Springfield 1, Massachusetts
February 10, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The report of Skau and Honold under the title "Moisture Regain of Tightly Woven Cotton Fabrics" [2] recalls a related experiment [1]. Two samples of cotton yarn, after exposure at high relative humidity, were brought to 65% RH at 21° C., where one sample was placed under a load of 60% of its breaking strength. The other sample was left unstressed. Moisture desorption regains after 24 hr. were stressed, 8.19%; unstressed, 8.78%.

The effect of loading is to tighten yarn twist, i.e., to increase the lateral compression of fibers above that in the unstressed yarn. This compression apparently reduces the regain, presumably by causing greater lateral fiber shrinkage.

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R. F. NICKERSON

Book Reviews

Natural and Synthetic Fibers Yearbook 1957. Edited by Milton Harris and H. Mark. New York, Interscience Publishers, Inc., 1958. 1144 pages. Price $45.00.

This volume comprises the abstracts originally published monthly during 1957, in loose-leaf form, for subscribers to the Interscience Textile Abstract Service. These abstracts differ in that they are far more complete and generally contain original data, graphs, charts, photographs, etc. Essentially they are digests which furnish sufficient information so that in many cases it is not necessary for a researcher to refer to the original article.

Articles to be abstracted are selected from the outstanding world publications and represent current progress in textiles throughout the world. The digests, in English, of articles which have appeared in foreign language publications will be particularly useful to many investigators. The bound and indexed volume makes the information easily accessible in libraries for reference purposes.

Planning of Experiments. D. R. Cox. New York, John Wiley & Sons. 308 pages. Price $7.50.

Reviewed by N. L. Enrick, Institute of Textile Technology, Charlottesville, Virginia

Research work in the experimental sciences and in industry can be greatly facilitated by the use of modern statistical methods of design and analysis, since they will usually extract a maximum amount of information from a relative minimum of experimental and testing work. A four-level latin square design, for example, can often yield more information with only 16 tests than a more conventional design involving 64 tests. "Planning of Experiments" presents a basic discussion of the various types of experimental design available to the research worker such as simple comparisons, randomized blocks, latin squares, factorials, sequentials, and response surface methodology.

Avoiding mathematics, the author relies on "intuitive reasonableness" for an explanation of the features and applicabilities of the various experimental designs, thus aiding the research worker in choosing that particular design which is most promising for a particular set of conditions.

Of the many examples on industrial applications, more than a dozen have been taken from textile mill and laboratory investigations. Other illustrations are drawn from physics, agriculture, medicine, and education. "Planning of Experiments" should thus be of interest to all research workers concerned with experimental investigations.

Drycleaning Technology and Theory. Albert R. Martin and George P. Fulton. New York, Interscience, 1958. 269 pages. Price $6.00.

Reviewed by C. H. Bayley, National Research Council of Canada, Ottawa, Canada

This book originally appeared in 1954 as a monograph prepared under a contract between the National Institute of Drycleaning, Silver Springs, Md., and the Research and Development Branch of The Office of the Quartermaster General of the U. S. Department of the Army. Its purpose, as given in the Preface, was "to give engineers, chemists and other technically trained personnel of that office a comprehensive survey of the science and technology of drycleaning."

The first chapter gives a general account of the development of drycleaning and, in concise fashion, sets the stage for the more detailed treatment which follows.

Chapter 2 covers soiling, natural and artificial, and gives an excellent presentation of a subject which, with respect to artificial soiling, still shows the effects of the early empiricism of approach. It is therefore gratifying to note the prominence which the authors give to the use of the Kubelka and Munk equation relating to the observed reflectance, the coefficient of reflectivity, and the coefficient of light scattering, since this has guided the quantitative studies of a number of workers in this field.

Chapter 3 deals with detergent processes in aqueous systems and comprises a treatment of the physical processes (i.e., wetting, emulsification, solubilization, etc.) usually encountered in a general treatment of this subject. Its inclusion in a book on dryclean-

ing is proper, both on the score of scientific treatment and also since wet processes are still in wide use by the drycleaning industry. Chapter 4 deals with the mechanism of soil removal in drycleaning and includes interesting data, hitherto unpublished, obtained at the National Institute of Drycleaning. This chapter also contains a useful treatment of the processes of soil suspension and solubilization as they relate to the drycleaning operation.

A full and highly informative treatment of drycleaning solvents is given in Chapter 5, which also includes sections on solvent care during use and on solvent recovery. A considerable amount of useful operating data is included here.

Chapters 6 and 7 deal with the detergents used in conjunction with solvents in drycleaning, the first of these chapters covering the older types of detergents, i.e., those based on soaps. This is followed by a discussion of synthetic detergents which, of course, form the bulk of the drycleaning detergents used by the industry today. The stressing of the importance of hydrophilic-hydrophobic balance is a feature of the second of these two chapters, this being of prime importance in a detergent, although the concept has still to be put into generally quantitative terms. A short section is included on analytical methods for the determination of moisture and of synthetic detergent in the drycleaning bath.

Having covered, in a general way, the subjects of the properties and manner and underlying principles of the use of the materials used in the drycleaning operation, the authors discuss in Chapter 8 the more important aspects of the colloid chemistry of the detergent bath, with special reference to micelle formation. This is followed by a discussion of the moisture equilibrium in the system solvent–water–surfactant (Chapter 9) and of the electrical conductance of the drycleaning bath (Chapter 10), these chapters covering adequately the present state of knowledge of the basic science relating to the current use of "charged" systems by the drycleaning industry.

The book concludes with a discussion (Chapters 11 and 12) of the scientific basis of garment finishing. While one must admire the temerity of the authors in attempting to draw attention to so many aspects of textile physics in so small a compass, we find that they say enough to whet the appetite and, through a bibliography, to motion the interested reader on to the sources of further knowledge; for not the least important feature of this useful book is its bibliography of 255 items.

The fact that this book contains a mixture of pure and applied science in no way detracts from its readability or its usefulness. The authors have reached the goal which they set themselves, and, in doing so, have produced a book which, because it discusses scientific principles at all, is unique among books on drycleaning. It deserves to be widely read by all interested in this important field which, incidentally, is one deserving of a greater degree of attention by textile scientists than it usually receives.